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FATS AND OILS

A SERIES OF MONOGRAPHS ON THE CHEMISTRY AND
TECHNOLOGY OF FATS, OILS, AND RELATED COMPOUNDS

SOAP
MANUFACTURE

IN TWO VOLUMES

J. DAVIDSOHN
CONSULTING CHEMIST, HAIFA, ISRAEL

E. J. BETTER
TECHNICAL DIRECTOR
SHEMEN ISRAEL OIL INDUSTRIES, LTD.
HAIFA, ISRAEL

A. DAVIDSOHN
CONSULTING CHEMIST, HAIFA, ISRAEL

VOLUME I

PREFACE

Until about the beginning of the present century, the production of soap was based on empirical knowledge slowly accumulated over many years. The theoretical principles, formulated during the last hundred years, have influenced the practical soapmaker for only about three decades.

It was fortunate for the industry that soap and its properties became of interest to students and investigators of colloid and other branches of physical chemistry. Many of the studies of the colloidal properties of matter were conducted with soap and soap solutions and, although not conducted with the primary purpose of solving the problems of the soap manufacturer, they initiated a trend toward employing scientifically trained personnel in the production and quality control of soap.

It was natural, therefore, that books devoted to the manufacture of soap would be addressed mainly to the practical soapmaker and their scope confined to process operations with little or no consideration for the theoretical principles involved. One of the first books which discussed the theoretical principles of soapmaking was *Lehrbuch der Seifenfabrikation* (Borntraeger, Berlin, 1928) by the senior author (J.D.) of the present work; it contained a brief chapter on this topic, and stressed throughout the theoretical principles underlying the various processes. Very few books in the English language can claim to supply the need for a detailed text on the subject of soap manufacture.

Since 1928 considerable progress has been made in our understanding of the structure of soap and soap solutions, of the phase behavior of soap, and the theory of detergency; also from the practical point of view, new manufacturing processes have been developed, new raw materials and builders have been introduced, and synthetic detergents have become an important factor in the soap industry. Because of these advances in the science and practice of soapmaking, a comprehensive treatise on the subject seems needed and the present two-volume work is an attempt to fulfill this need.

The first six chapters of Volume I are devoted to the theoretical principles that require understanding as a foundation for studying the practical soap processes which are described in the subsequent chapters. Other chapters of this volume deal with the raw materials used in the industry.

The second volume is devoted in part to a description of equipment, design, and operations conducted on the soap-boiling floor and in those departments in which soap is converted into its final shape. The problems of general technical administration are also discussed in this volume. The properties of soap and soap solutions which influence performance are discussed, and brief descriptions of the main classes of synthetic detergents are presented. The remainder of Volume II deals with the recovery of glycerine and with the analytical control of raw materials and finished products. It was deemed advisable to add an appendix consisting of two chapters devoted to laboratory soapmaking which is intended primarily for the non-apprentice student who has not had practical soap-boiling experience. The practical soapmaker may have little interest in these chapters, but on the other hand he may find them helpful in indicating the ease with which the laboratory can provide information applicable to full-scale operation with greatly lessened risk and economy of time and materials.

The authors are grateful to John McCutcheon for reading and revising their manuscript, to Klare S. Markley for reading the proofs and making invaluable suggestions for improvement of the text, and to the publishers for the opportunity to present this work to the public.

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J. DAVIDSOHN
E. J. BETTER
A. DAVIDSOHN

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July, 1953

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HISTORY AND STATISTICS
OF THE SOAP INDUSTRY

(1) History

Soap has been known for at least 2300 years. Indeed, some authorities suggest that the Phoenicians made soap in 600 B.C., and used it as an article of barter with the Gauls. According to Pliny the Elder it was prepared from goat's tallow and wood ashes. In the period of the Roman Empire the use of soap became quite popular. But it is still not known whether the Romans learned to use and to manufacture soap from the ancient Mediterranean peoples or if they learned it, as some people believe, from the Celts, the inhabitants of Britannia. The Celts produced soap from animal fats and plant ashes, which served as alkali. They gave this product the name "saipo," from which the word "soap" is derived. The importance of soap as a means of washing and cleasing does not seem to have been recognized until the second century; it is the Greek physician Galen (about 130–200 A.D.), who mentions soap as a medicament and a means of cleansing the body. According to the physician Theodorus Priscianus (about 385 A.D.), soap was used as a shampoo, and he is the first to mention the profession of the "Saponarius," or soap boiler.

About 800 A.D., the celebrated Arab chemist, Jabir ibn Hayyan (Geber), the "father of alchemy," repeatedly mentions soap as an active means of cleansing in his writings.

After the fall of Rome the history of soap is very scantily recorded. In the Middle Ages the center of soap production was at Marseilles. Later on the mantle passed to the cities of Genoa and Venice. It is often claimed that soap manufacture in the Middle Ages was developed mainly in Germany, but this seems unlikely, as the use of soap in Central Europe at that time and even

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later was so unusual that a box of soap presented to the Duchess of Juelich in 1549 caused quite a sensation; and even as late as 1672 when the German, A. Leo, sent Lady von Schleinitz a parcel with soap from Italy he accompanied it with a detailed description of how to use this mysterious product.

The first English soap-maker probably lived at the end of the twelfth century in Bristol, where the soap was then being made. In the thirteenth and fourteenth centuries a small community of soap makers grew up in the neighborhood of Cheapside, in London. In those days the soap makers had to pay a duty on every ton of soap they produced. After the Napoleonic Wars the tax was as high as three pence on every pound of soap, and the soap-boiling pans were fitted with lids that could be locked every night by the tax collector in order to prevent production under cover of darkness. It was not until 1853 that this high tax was finally abolished—at a sacrifice to the state of over a million pounds sterling. It is easily seen from this that soap was used to a great extent at that time.

In an article on the development of the so-called "Marseilles soap," E. Maurel[1] presents some interesting historical facts. Soap makers in this famous town of early soapmaking kept their processes secret, and not even the Academy of Marseilles in 1769 could induce them to reveal their secrets when they offered a prize for a paper on the best way to manufacture soap. It was not until five years later that a paper was finally submitted, but it was not the work of a member of the trade. It was written by a layman who admitted frankly that the subject matter had been confided to him by a friend who was a soap maker. On the eve of the French Revolution the production of soap from Marseilles had already reached the figure of 3500 tons per year —a respectable one for those days—produced by thirty-four small factories.

Trademarks on the pieces of soap and on the packing cases date from the end of the eighteenth century. From this time onward the Marseilles industry began to export (chiefly to America) quantities of soap which for that era attained no mean figure.

Production mounted steadily, and according to one author there were 140 boilers at Marseilles in 1760, 152 in 1775, 236 in 1789, and 360 at the beginning of the First Empire. The manufacture of artificial soda by the LeBlanc process, discovered at this time (1804), gave a real impetus to the soap trade.

In earlier times Marseilles soap was produced mainly from olive oil. In the time of the Restoration, about 1815, a number of poor olive harvests hampered the Marseilles soap industry, which had to look for other oils for soap

[1] E. Maurel, *Corps Gras*, January, 1944, through *Soap Perfumery & Cosmetics*, **19**, 289–290 (1946).

production. Soap makers were induced to use more and more seed oil, and the parallel development of steam navigation and improvements in colonial ports could provide oils in increasing quantities each year. This had the effect of changing the soap formulas, and, as is done today, fat and oil stocks were carefully blended from seed oils, tallow, and coconut oil.

The use of soap became common indeed in the last century. Justus von Liebig, the famous German chemist, declared in the second half of the century that the quantity of soap consumed by a nation would be no inaccurate measure of its wealth and civilization, and that, of two countries with an equal amount of population, the wealthiest and most highly civilized would consume the greatest weight of soap.

In this connection, Table I-1 may be of interest. It must be mentioned that recent statistics in the U. S. show a certain decline in the per capita consumption of soap, *i.e.*, 9.6 kg. per year in 1951. This is probably caused by the increased use of synthetic detergents.

TABLE I-1

PER CAPITA CONSUMPTION PER YEAR OF SOAP (IN 1931)

Country	Consumption	
	Pounds	Kilograms
United States	25	11.4
Netherlands	24	10.9
Great Britain	20	9.1
France	17	7.7
Germany	13	5.9
Japan	7	3.2
Brazil	6.8	3.1
Russia	5.7	2.6
India	4.0 oz.	0.12
China	2.0 oz.	0.06
World average	*6.6*	*3.0*

Soap-boiling methods probably evolved through the centuries along the following lines. First, simple wood or plant ashes containing potassium carbonate was dispersed in water, and fat was mixed into the solution. This was then boiled, the water evaporated, and ash added again and again to the "soap kettle" on the fire. During this process a slow splitting of the neutral fat occurred; the fatty acids could then be saponified with the alkali carbonates. Animal fats containing a percentage of free fatty acids were used by the Celts. The presence of free fatty acids certainly helped to get the process started. This method very probably prevailed until the end of the Middle

TABLE I-2

QUANTITY (IN THOUSANDS) OF PRODUCTS, TOTALS FOR THE UNITED STATES IN 1947

Product	Quantity produced, thousands
Soap, except specialty soap:	
Bars:	
Toilet	565,617 lb.
Laundry and household:	
White	406,561 "
Yellow	358,329 "
Other (including industrial)	28,105 "
Chips and flakes:	
Packaged	227,961 "
Bulk	195,106 "
Granulated, powdered and sprayed:	
Packaged	1,412,458 "
Bulk	133,989 "
Washing powder:	
Packaged	84,839 "
Bulk	106,318 "
Cleansers, containing absasives:	
Packaged	267,087 "
Bulk	77,185 "
Liquid, excluding shampoos (potash and other):	
Packaged	2,247 gal.
Bulk	14,454 "
Paste and jelly (potash and other):	
Packaged	12,931 lb.
Bulk	33,015 "
Specialty soaps:	
Shaving cream lather:	
Tube	9,049 "
Jar	265 "
Shaving soap	6,348 "
Glycerine (100% basis):	
Crude	206,186 "
High gravity, dynamite, and yellow distilled	86,943 "
Chemically pure	103,900 "
Synthetic organic detergents:	
Not in combination with soap or other detergents:	
Liquid:	
Packaged	853 gal.
Bulk	3,783 "
Solid:	
Packaged	243,734 lb.
Bulk	14,849 "
In combination with soap:	
Liquid:	
Packaged	397 gal.
Bulk	1,040 "
Solid, packaged and bulk	17,304 lb.
In combination with alkaline detergents:	
Liquid:	
Packaged	82 gal.
Bulk	1,138 "
Solid:	
Packaged	23,548 lb.
Bulk	58,992 "
Alkaline detergents:	
Solid:	
Packaged	96,030 "
Bulk	297,090 "

Ages. Then came a new development with the process of causticizing of the alkali carbonate with slaked lime. Through this process, neutral fats could be saponified easily with the caustic lye deriving from the process of causticizing.

Since the ash from land plants gave only potassium carbonate the soaps manufactured in Central Europe were a type of soft soap. The soap industry in coastal towns could use ash from sea plants which contain sodium carbonate. Thus, a hard soap could be produced in Marseilles, Genoa, and other coastal towns. It is possible that at many places in Europe the soft potash soap was transformed into hard sodium soap by treatment with brine solution. Unfortunately, we do not know when the process of "salting out" was invented, but it is very likely that it is centuries old. With the invention of the LeBlanc soda process cheaper sodium carbonate became available and hard soap became the important product it is today.

Another factor helped to develop the soap industry. It was the work of the French chemist, Chevreul, who in 1823 showed that the process of saponification is the chemical process of splitting fat into the alkali salt of fatty acids (that is soap), and glycerine.

The introduction of soap boiling with open steam at the end of the 19th century was another step on the road of soap production from a handicraft to an industry.

Many other developments of a technical nature also had a great influence on the industry as a whole: the introduction of rosin in the soap kettle about 1850; the use of sodium silicate by Gossage in England about 1870; the hydrogenation of oil to suitable soap-making fats just after the turn of the century. Technical developments during World War I may be said to hinge on the processes for oil polymerization, on the production of synthetic fats from hydrocarbons, and on the new type of synthetic detergents. This last did not receive world-wide prominence until after World War II. It is still too early to form any immediate evaluation, although it would appear that of 4000 million pounds of detergents sold in 1948 approximately 3200 million pounds comprised soap, and 800 million pounds comprised synthetics.[2]

Last, but perhaps of far greater significance to the soap industry, are the new continuous methods of saponification and boiling that are being used at the present time in all parts of the world.

(2) Statistics

In 1939, 595 United States soap plants provided employment for 17,349 persons in the production of soap valued at $302,634,474.

The data in Table I-2 from the 1947 U. S. Census of Manufacturers show the rapid growth of synthetic detergents in this field.

Now to consider some figures which illustrate energy consumption in the soap industry as represented by fuel and electricity purchased in terms of per cent of total value of products:

	Fuel, %	Electricity purchased
All chemical process industries in U. S., average	4	1
Soap industry in U. S.	0.75	0.25[3]

The cost of labor that goes into the value of products is below 20% in the soap industry in comparison to more than 50% in coal mining, 40–50% in steel production, 30–40% in the textile industry and in the machine tool industry, 25–30% in chemicals-producing industry, and 20–25% in the petroleum industry. Thus it is seen that labor represents a smaller than usual portion of the cost of soap products.

A chart of operating ratios for 2688 firms in 89 industries, including soap, was prepared from data compiled by the U. S. National Industrial Conference Board based on studies made by the Federal Trade Commission of corporate reports for the year 1940 (a rather normal year for the U. S.[4]). Table I-3 lists the ratios for the 20 soap companies whose costs were analyzed:

TABLE I-3

	Per cent per sales dollars	Position
Raw material	50.35	18
Direct labor	3.44	89
Indirect labor	2.53	71
Depreciation	1.25	75
Repairs and maintenance	1.43	65
Other costs and finished goods	4.22	74
Corporate taxes	2.93	2
Social Security and pension fund payments	0.49	88
Research and development	0.55	31
Selling and delivery	8.89	34
Advertising	10.94	4
Administrative and general office expenses	2.30	78
Uncollectable accounts	0.16	43

Now something about the safety factor in the soap industry. Table I-4 lists the disabling injuries in the United States in 1939 for all the chemical industries compared with corresponding figures in the soap industry alone.[5]

[2] R. N. Shreve, *The Chemical Process Industries,* McGraw-Hill, New York, 1945, p. 63.

[3] Distributed by Association of American Soap and Glycerin Producers, Inc.

[4] R. N. Shreve, *ibid.,* p. 35.

From these figures it is evident that safety in the soap industry leaves something to be desired as compared to the average in all chemical industries.

TABLE I-4

	All groups	Laboratories	Cl$_2$ and alkali mfg.	Soap mfg.	Vegetable oil mfg.
Number of industrial units	417	13	12	31	30
Man hours worked, thousands	305,535	4,202	15,206	24,760	7,609
Av. number of employees	144,378	2,062	6,645	12,556	3,850
Number of disabling injuries					
Death and permanently totally disabling	40	0	2	2	0
Permanent partially disabling	172	0	3	32	9
Temporary totally disabling	2,073	3	57	234	131
Total	*2,285*	*3*	*62*	*268*	*140*
Injury rates					
Frequency	7.48	0.71	4.08	10.82	18.40
Severity	1.26	0.003	0.96	1.32	1.42
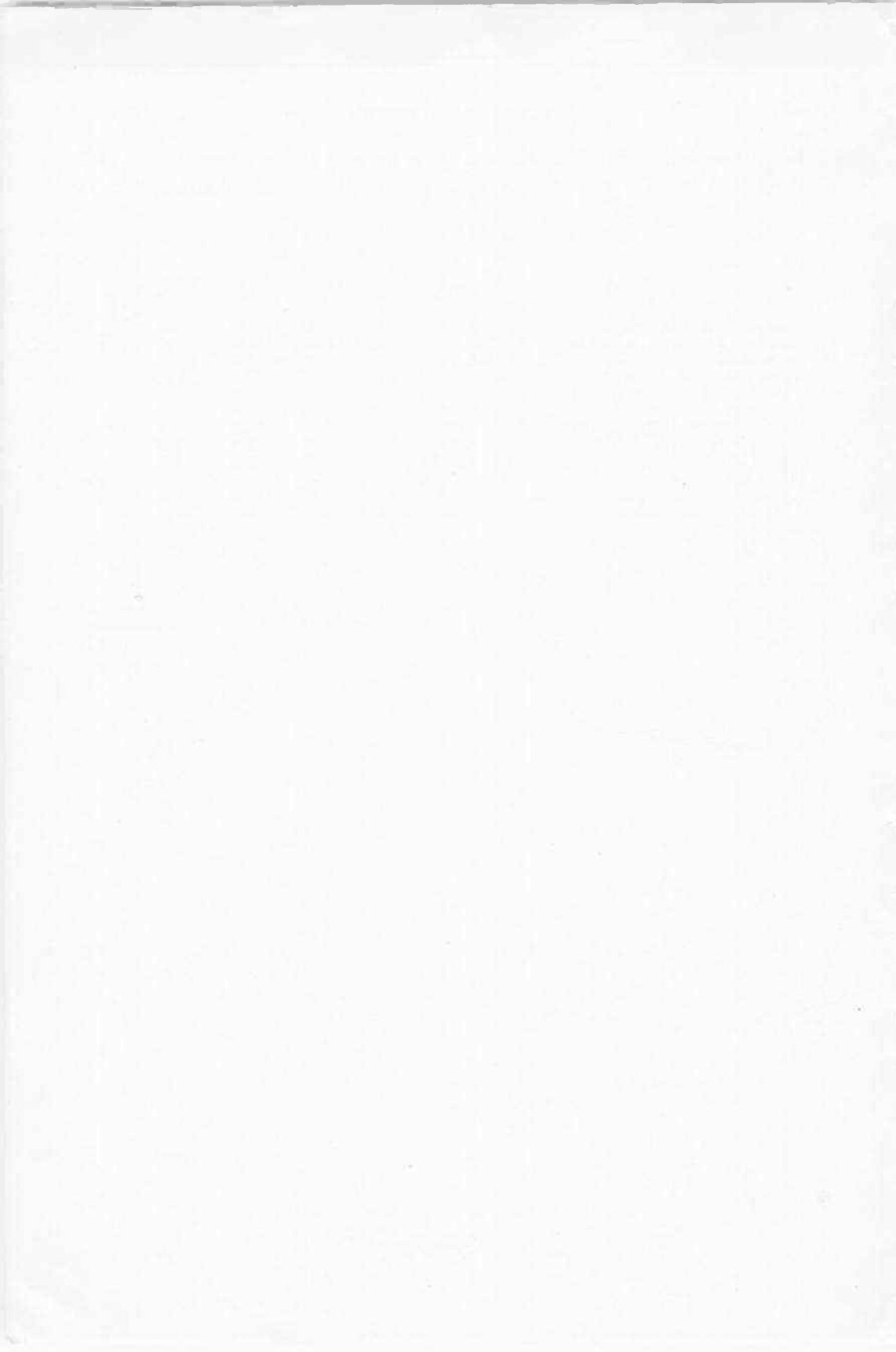
PART A

Theoretical Principles of Soap Manufacture
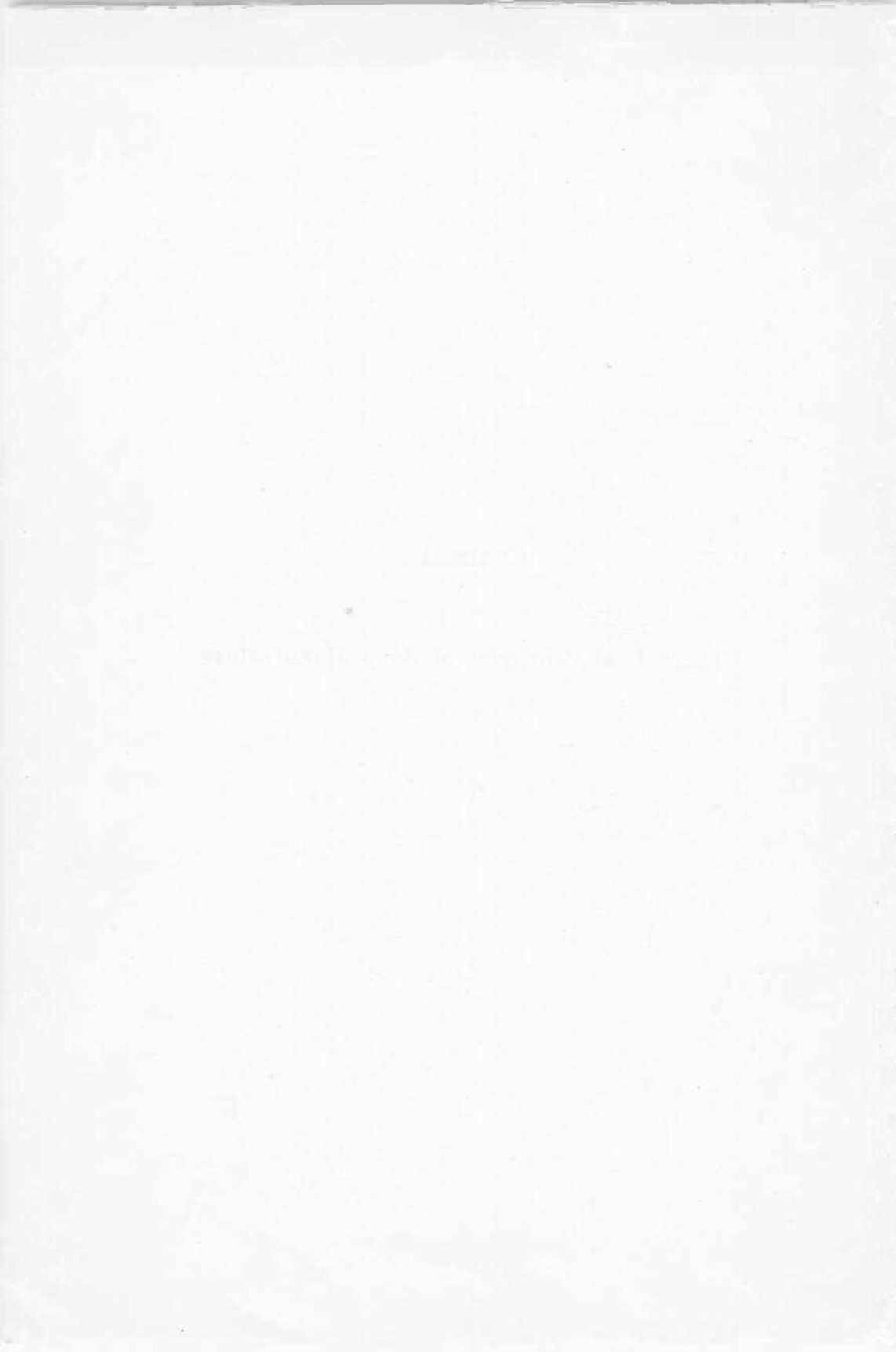
Introduction

In a strictly chemical sense, any compound formed by the reaction of a water-insoluble fatty acid with a metallic radical or with an organic base may be called a "soap." Practically, however, the soap industry is concerned mainly with those water-soluble soaps which result from the interaction between fatty acids and alkali metals. It must be pointed out, though, that in certain cases the salts of fatty acids with ammonia or with triethanolamine are also used as technical soaps (*e.g.*, in shaving preparations).

In addition to the fatty acids proper, abietic acid and the naphthenic acids are also capable of forming salts with alkali metals, and these compounds are water soluble and display "soaplike" properties.

Salts of fatty acids with heavy metals or with alkaline earth metals are water insoluble and are, as a rule, termed "metallic soaps." They possess no detergent or soaplike properties.

The process which takes place when a soap is formed from a fatty acid and an alkali metal by the action either of a caustic alkali on a neutral oil or on free fatty acid, or of an alkali carbonate on a free fatty acid, is called *saponification.* A neutral oil is a compound of three molecules of fatty acids with one molecule of glycerine. Such compounds are termed *esters,* and in this special case *triglycerides.* Whenever the soapmaker uses the term *saponification* he means that three molecules of soap have been formed and one molecule of glycerine liberated from one molecule of triglyceride by the action of three molecules of alkali. The term is, however, also applicable to a process in which only one molecule of free fatty acid and one molecule of alkali are involved, but in which only one molecule of soap is formed.

The following equations represent the saponification of triglyceride by sodium hydroxide (1) and the saponification of free fatty acid by sodium hydroxide (2) and by sodium carbonate (3).

It will be necessary to keep in mind that, in organic chemistry, the use of the term saponification is not restricted to the above described combinations of alkali with free fatty acids or the splitting of a triglyceride by caustic alkali. In the broader sense the term covers the splitting of an ester (reaction product of an alcohol and an acid) into its components by the action of alkali or acid, or simply by water. Accordingly, the process of splitting a neutral

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fat into fatty acids and glycerine by any of the known technical processes (by autoclaving, by Twitchell reagent, or by the fermentation process) would also be termed a saponification process. The term saponification for reac-

$$
\begin{array}{ll}
\text{(1)} &
\begin{array}{l}
CH_2OOC-(CH_2)_{16}-CH_3 \\
CHOOC-(CH_2)_{16}-CH_3 \quad + \quad 3NaOH \quad \rightarrow \\
CH_2OOC-(CH_2)_{16}-CH_3
\end{array}
\begin{array}{l}
CH_2OH \\
CHOH \quad + \quad 3CH_3-(CH_2)_{16}-COONa \\
CH_2OH
\end{array}
\end{array}
$$

      Stearic acid—triglyceride   Caustic soda   Glycerine   Sodium stearate
       (Mol. wt. 890)   (Mol. wt. 40;   (Mol. wt. 92) (Mol. wt. $3 \times 306 = 918$)
                      $3 \times 40 = 120$)

(2) $CH_3-(CH_2)_{16}-COOH + NaOH \rightarrow CH_3-(CH_2)_{16}-COONa + H_2O$

         Stearic acid   Caustic soda   Sodium soap   Water

(3) $2CH_3-(CH_2)_{16}-COOH + Na_2CO_3 \rightarrow 2CH_3-(CH_2)_{16}-COONa + CO_2 + H_2O$

        Stearic acid   Sodium   Sodium soap   Carbon   Water
                    carbonate   dioxide

tions which fail to lead to the formation of soap is undoubtedly a misnomer and it would be more correct to call such ester-splitting reactions *hydrolysis*. In the following, the term saponification will be used exclusively for reactions that result in the formation of soap.

THEORETICAL ASPECTS OF SAPONIFICATION OF FATS WITH CAUSTIC ALKALI SOLUTIONS

(1) Neutralization of Free Fatty Acids

Caustic alkali solutions react spontaneously when brought into contact with free fatty acids, and soaps are formed almost immediately. Stoichiometrically equivalent quantities of the two components, *e.g.*, 282 grams of oleic acid and a solution of 40 grams of caustic soda, will form a solution of 304 grams of soap at any temperature, provided that care is taken for adequate mixing and agitation. The saponification reaction between fatty acids and caustic or other alkalis is an exothermic process. The heat generated by saponification of one molecule of fatty acid—the molecular heat of neutralization—amounts to about 14 calories.

It would appear from equation (4) that free fatty acids could be com-

(4) $$2R-COOH + Na_2CO_3 \rightleftharpoons 2R-COONa + H_2O + CO_2$$

pletely saponified at any temperature by alkali carbonates as well, provided that the liberated carbon dioxide is separated continuously from the reaction product. However, at low temperatures carbon dioxide is able to liberate the free fatty acid from dilute soap solutions, a reaction which takes place at higher temperatures, only to a very small extent. For this reason, the complete neutralization of a fatty acid by alkali carbonate solutions can be carried out in a practical way only at boiling temperature. In principle, neutralization with alkali carbonates could be carried out at lower temperatures only if the liberated carbon dioxide could be eliminated by means other than boiling, *e.g.*, by application of a vacuum or by strong agitation with mechanical means or even by air.

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(2) Saponification of Neutral Fats

Reactions between neutral fats (triglycerides) and alkali carbonates do not occur readily under current technical conditions. Even the reactions between caustic alkali and neutral fats do not start spontaneously. For the initiation of reactions of this kind, certain conditions must be fulfilled. The saponification reaction will start when:

(*a*) Fats containing low molecular weight fatty acids (coconut oil, palm kernel oil, etc.) are agitated with highly concentrated (above 38° Bé) caustic alkali solutions at low temperatures.

(*b*) When oil or fat is emulsified with concentrated alkali by intensive agitation in the cold.

(*c*) When oil or fat is mixed with concentrated caustic alkalies at low temperature in the presence of a suitable catalyst.

(*d*) By mixing preheated fats and concentrated caustic alkalies and maintaining an elevated temperature (around 90° C.) during agitation.

(*e*) By boiling fats with aqueous caustic alkalies of various concentrations.

(*f*) By heating fats with alkalies under pressure.

(*g*) By heating fats with water-free alkalis in the presence of solvents.

(3) Heat of Saponification of Neutral Fats

When saponification starts under any of the above sets of conditions, heat is always evolved as a result of the reaction. This fact is utilized in the "cold-made" soap process.

As was pointed out by Lascaray,[1] the total reaction heat of the alkali saponification of fat must be regarded as composed of: (*1*) the molecular heat of hydrolysis of a triglyceride and (*2*) the molecular heat of neutralization of the fatty acid. The heat of hydrolysis for one mole of triglyceride has been established at 18 Calories. The molecular heat of neutralization is 14 Calories. The saponification of 1 mole of triglyceride will therefore yield $18 + (3 \times 14) = 60$ Calories. This means that the comparatively small molecule of coconut oil (molecular weight about 680) and the large molecule of olive oil (about 880) will produce the same amount of calories when transformed into soap; however, 1 kg. of liquid coconut oil will produce $60 \div 0.68 = 88$ Cal. and 1 kg. of olive oil $60 \div 0.88 = 68$ Cal. when transformed into soap by alkali saponification.

[1] L. Lascaray, in Hefter-Schoenfeld, *Chemie und Technologie der Fette und Fettprodukte*, Vol. IV, Springer, Vienna, 1939, p. 172.

(4) Kinetics of Saponification

(A) Saponification a Bimolecular Reaction

In order to acquaint ourselves thoroughly with the phenomena of a chemical reaction we must study its course as it progresses at various temperatures and through a sufficient period of time. The rate at which a chemical reaction proceeds is proportional to the concentration of the reacting substances. In the saponification reaction there are two kinds of molecules involved—the triglyceride and the saponifying alkali. The mathematical expression of this reaction must have different characteristics as compared with the reaction which involves, for instance, only the decomposition of a single molecule, or with the reaction in which more than two kinds of molecules take part.

Ordinary fats and oils are practically insoluble in water or in caustic alkali, and therefore the reaction mixture must be regarded throughout the whole process as essentially heterogeneous. In spite of this conception of heterogeneity, fat is to some small extent dissolved in the caustic alkali solution, and the saponification is restricted to this homogeneous part of the system. Under this circumstance the rate of saponification will be the sum of two components: the velocity with which the fat is dissolved in the caustic solution and the velocity with which this dissolved fat is saponified in homogeneous solution. The second of these components, the rate of the chemical reaction taking place in solution, must be assumed to follow the laws established for molecular reactions. This assumption is supported by experiments with the water-soluble acetic acid esters of glycerine.

Let us call the concentration of an ester before saponification has taken place "A" and the concentration of the alkali present at the same time "B." After a certain period of time has elapsed, say t minutes, the alkali will have reacted upon the ester and the remaining portions of ester and alkali are called, in terms of concentration, "C_1" and "C_2," respectively. The saponification of glyceryl monoacetate with a 0.02 N caustic potash solution has been studied[2] very accurately at two temperatures, 18 and 25° C. The reacting mixture was analyzed after 8, 11, 15, 25, and 30 minutes and the values for C_1 and C_2 were tabulated.

Since A and B were known, it could be shown that the values for t fit into the following equation:

$$\frac{1}{t}\frac{1}{A-B}\ln\frac{BC_1}{AC_2} = k$$

[2] J. Meyer, in Ubbelohde-Heller, *Handbuch der Oele und Fette*, Vol. 3, Hirzel, Leipzig, 1930, p. 3.

This is the mathematical expression for a bimolecular reaction, and is confirmed because the experimental values for C_1 and C_2 satisfy this formula. k is a constant for any given temperature, and for any value of t it is called the reaction velocity constant or, in this case, the saponification constant. k depends only on the saponification temperature. Since the value of k is known, it is possible to calculate how far saponification has progressed at a given time. If k is calculated for two different temperatures, the influence of temperature on the velocity of saponification may be determined.

In the case above, k was found to be 8.05 at 18° C. and 17.05 at 25° C., which means that the velocity of the reaction is more than doubled by increasing the temperature by 7° C.

The soapmaker deals with triglycerides or ester compounds in which one molecule of glycerine is bound with three molecules of fatty acids. In such a compound there is at least one position, the secondary OH group, which can behave differently from the two primary positions:

$$CH_2OCOR \quad \text{(primary)}$$
$$CHOCOR \quad \text{(secondary)}$$
$$CH_2OCOR \quad \text{(primary)}$$
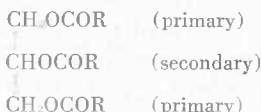
The saponification velocity of the secondary group has been reported to be different from that of the primary ones. However, when the course of the saponification reactions of glycerine di- and triacetates, as well as that of monoacetate, was studied as described previously, primary and secondary group constants were found to be almost identical. This serves as proof that all three ester groups in the triglyceride molecule are saponified by caustic alkalies at the same rate when all other conditions are the same.

(B) The Gradual Course of Saponification of a Triglyceride

The foregoing should not be misinterpreted by assuming that the saponification of a triglyceride progresses by a simultaneous attack on all three ester groups. Such a mechanism would involve four molecules (one glyceride and three alkali molecules), and would therefore represent a tetramolecular reaction. The experimentally observed bimolecular mechanism clearly indicates that saponification starts by splitting off one of the three fatty acids from the triglyceride molecules and that the diglyceride thus produced is subsequently partially saponified into another molecule of soap and a monoglyceride. It is then the monoglyceride which is finally saponified to produce free glycerine and a third molecule of soap.

As to the velocity with which the various stages are transformed into one another, it is very likely that the rates of saponification of tri-, di- and mono-

ester are in the ratio 3 : 2 : 1, respectively. The following formulas illustrate the possible transformations:

$$CH_2OCOR$$
$$CHOCOR$$
$$CH_2OCOR$$

$$k_1 : k_2 : k_3 = 3 : 2 : 1$$

$$CH_2OH$$
$$CHOH$$
$$CH_2OH$$

+ 1 mole soap
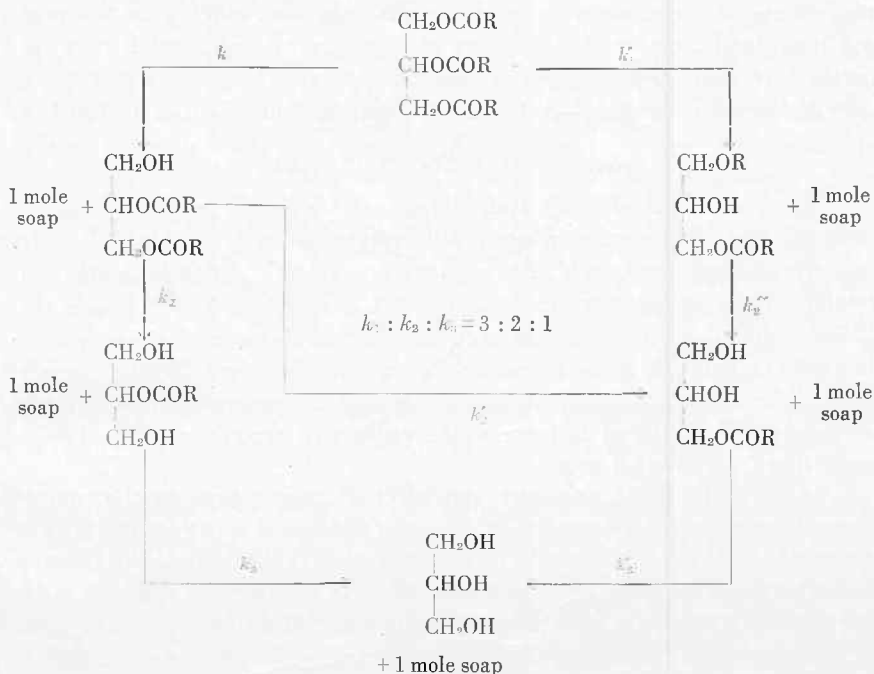
(C) Is Saponification of Fats a Homogeneous or Heterogeneous Reaction?

Until now, only such kinetic studies were discussed which were carried out as model reactions on the water-soluble acetic acid esters of glycerine. There was a great deal of controversy about whether or not the ordinary fats follow the same course of reaction as established on the homogeneous models, in spite of being insoluble in water or caustic alkali solutions.

One of the arguments against the theory of the gradual course of saponification was that, in view of the fact that mono- or diglycerides have never been found as such in saponification mixtures, it is unlikely that such products should indeed be involved in the course of the saponification of ordinary fats. Davidsohn[3] did show, however, that in products of cold process saponification the unsaponified fat always contains mono- and diglycerides.

It has been explained that the originally water-insoluble fat must somehow find its way first into the water–caustic phase prior to its saponification.

[3] J. Davidsohn, *Seifensieder Ztg.*, Augsburg, *1927*, Nos. 16 and 17. Also K. L. Weber, *ibid.*, *1921*, p. 3.

A diglyceride of a water-insoluble fatty acid is much more water soluble than its triglyceride, and a monoglyceride is even more so. Thus, one would expect mono- or diglycerides to be absorbed much more quickly by the aqueous phase and therefore to disappear at a greater rate of speed than would be the case with a triglyceride. This probably explains the fact that mono- and diglycerides were seldom found in saponification mixtures in practice.

(D) Saponification Velocity and Temperature

The general rule of Van't Hoff states that with each temperature increment of 10° C. the reaction velocity will be approximately doubled. For the saponification of acetic acid, the reaction rate was shown to be more than doubled for a temperature increase of 7° C. (see Sect. 4A). Norris and McBain[4] found for soybean and coconut oils that the rate of saponification increases 1.3 to 1.6 times when the temperature is raised 10° C. Smith[5] studied the cold saponification of cod liver and coconut oils and found that an increase of 20° C. could increase the velocity of saponification by two to eight times the original rate.

According to Smith, however, the effect of temperature on the rate of saponification must be regarded as not being controlled solely by the laws of chemical kinetics. The net rate of saponification is determined, in addition to temperature, by other factors as well; these factors may be summed up as the physical state of the soap at any given moment of the saponification process. The solubility of oil and alkali in the soap, as well as the rate of diffusion of oil and alkali in the soap, are dependent on the physical condition of the soap particles. This physical condition, in turn, is a function of temperature, and the variation of physical conditions with temperature will thus also indirectly affect the rate of saponification.

(5) The Stages of the Saponification Reaction

(A) General

Even by assuming that very small quantities of fat can be dissolved in the caustic alkali solution, this cannot fully explain certain very high saponification velocities that may be observed in practice. On the other hand, the possibility of saponification taking place in the fat was denied because OH ions are known to be practically absent from the fatty phase. Therefore, it had to be assumed that the reaction occurs preferentially on the interface of the emulsion between the fat and caustic alkali solution.

Norris and McBain[4] studied the saponification of coconut and soybean oil, triolein, and tripalmitin by boiling these oils with caustic alkali solutions

[4] M. H. Norris and J. W. McBain, *J. Chem. Soc. London, 121* and *122*, 1363 (1922).
[5] E. L. Smith, *J. Soc. Chem. Ind., 51*, 337T (1932).

under reflux and determined the rate of reaction. They found that the initial velocity was low; then came a period of very rapid saponification; and at the end the rate of reaction decreased considerably. Agitation at the beginning increased the rate of reaction of the first, otherwise very slow, phase to twenty times the original rate. This seems to indicate that the first phase of saponification depends to a very large extent on the degree of emulsification between the fat and caustic solution. The practical soapmaker is well acquainted with these three phases in soap boiling, as described by McBain and his associates on the basis of their studies of saponification kinetics. While in the first slow period the reaction rate seems to depend on the proper state of emulsion existing between the components, in the second stage, during which saponification progresses very quickly, the reaction seems to proceed not at the emulsion interface but in solution.

(B) THE EMULSION PHASE

It is well known that the stability of an emulsion is greatly affected by the presence of an emulsifier between the components. In our case, the soap itself serves as an excellent emulsifier for oil-in-water emulsions. The saponification mixture will therefore represent, in its first stage, a system in which oil globules are more or less finely dispersed in the caustic alkali solution. This stage will not be reached at once, and prior to the formation of the emulsion sufficient amounts of soap must be formed so that it can enter into its role as an emulsifier. This formation of the initial quantities of soap will probably proceed according to the rules stated above, that is, by gradual formation of the whole range of glycerides.

However, the soap cannot act as an emulsifier when the presence of excess alkali or of other electrolytes interferes with its solubility in water. It will be seen later that the soaps of certain fats are extremely susceptible to influence of electrolytes and are liable to be "grained out" by concentrations of salt or caustic as low as 4 to 5%. Such oils are olive oil, peanut oil, and tallow; while coconut oil and castor oil are far less susceptible. "Graining out" means that the soap loses its solubility in water and is precipitated as a curd containing 30% or less occluded water.

In the interest of good emulsification, it is therefore most essential that, at the beginning, an excess concentration of alkali or other electrolyte should not be used. Otherwise, at a certain maximum limit of electrolyte concentration the soap would be grained out and the emulsion would cease to exist, and the rate of saponification would drop at once to a very considerable extent. In the case of coconut oil the emulsion is able to withstand much higher caustic concentrations than in the case of, say, tallow. At any rate it is always good practice to start the addition of caustic by first adding weak solutions or by making sure that sufficient water had been added to the oil at the

beginning so as to dilute the strong alkali. If too high a concentration of alkali accidentally enters the saponification mixture at any time during the saponification, it is good practice to stop agitation and boiling. The layers will eventually separate and the fat layer will consequently contain less alkali; but the fat layer will retain some soap and saponification will then proceed much more quickly in this separated layer than in the presence of large excesses of alkali. Eventually the emulsion will take on the character of a fully homogeneous mass and the rate of reaction will quicken, showing that the saponification has entered a new phase.

(C) The Autocatalytic Role of Soap Micelles

This new phase is recognized by the outward appearance of the soap-lye-fat emulsion, which becomes more or less transparent at this stage although it still contains large quantities of unsaponified fat.

It was known for some time that aqueous soap solutions are able to dissolve fats and other organic substances, and it was emphasized by Pickering,[6] Hartley,[7] and Smith[8, 9] that such systems are true solutions and not emulsions. It was shown later by some of these investigators that fat can be dissolved by a soap solution only when the soap concentration is above a certain minimum limit, and that above this minimum concentration the solubility of fat in the soap solution remains constant.

The explanation given by Hartley for this phenomenon was that soap solutions, when above the observed minimum concentration, contain "soap micelles" which are able to dissolve fats. According to Hartley, these micelles consist of fatty acid ions aggregated into one spherical drop in such a way that the carboxyl groups at the end of the paraffin chain point outward toward the water, while the remainder of the paraffin chain remains oriented more or less in the direction of the center of the drop. The carboxyl group is hydrophylic, while the paraffin chain of the fatty acid behaves like a pure hydrocarbon and is therefore insoluble in water and tends to withdraw from the solution. The center of such a micelle would consequently behave similarly to a drop of paraffin or other solvent and be able to dissolve fat. This concept is now generally accepted, with the modification suggested by McBain,[10] who replaces Hartley's spheric concept with what he calls a "lamellar micelle." See Figures II-1, 2.[11] In such a lamellar micelle the oil is sandwiched in the hydrocarbon layers between parallel planes of soap molecules.

[6] S. U. Pickering, *J. Chem. Soc. London*, *111*, 86 (1917).

[7] Hartley, *Wetting and Detergency*, London, 1937, p. 161.

[8] E. L. Smith, *J. Phys. Chem.*, *36*, 1401, 1672 (1939).

[9] E. L. Smith, *ibid.*, 2453.

[10] J. W. McBain, in *Advances in Colloid Science*, Vol. I, Interscience, New York, 1942, p. 118.

[11] K. Tomlinson, *Manufacturing Chemist*, *15*, 199 (1944).

It was possible to introduce direct evidence by x-ray diffraction concerning the manner in which soap solution solubilizes the hydrocarbon benzene. It was shown that the length of an anhydrous sodium oleate molecule is 24.5 angstrom units (1 A. $= 1 \times 10^{-7}$ mm.), and it was found that the lamellar micelles formed by two layers of sodium oleate measured 91 A. The increased spacing is due to the incorporation of an aqueous layer 42 A. thick between the two layers of anhydrous soap.[12] When benzene is solubilized in the sodium oleate solution, the lamellar micelles expand to incorporate sheets of solubilized molecules between the hydrocarbon ends of the soap layers, and the x-ray spacing increases from 91 to 127 A. (See Figure II-3.[12])
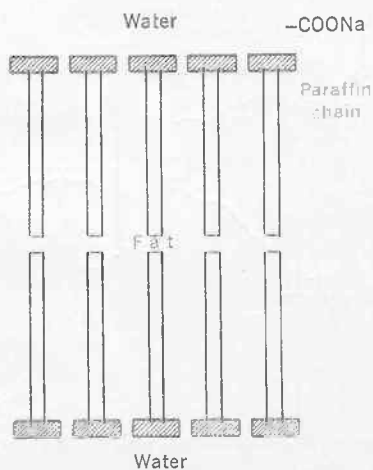
Fig. II-1. Lamellar micelle.[11]   Fig. II-2. Spheric micelle.[11]
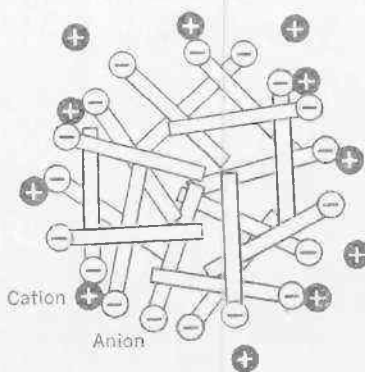
Smith[13] first drew our attention to the possibility that during the period of rapid saponification and when approaching the stage of semitransparency, the fat might actually be dissolved in the soap globules present in the solution. He investigated the rates of the reaction of cod liver oil and of coconut oil with aqueous solutions of sodium and potassium hydroxides of varying concentrations at 25 and 45° C. In spite of the fact that these conditions correspond to cold saponification the results are applicable also to the method of soap manufacture by boiling. We have stated, when explaining the conditions prevailing during the saponification in emulsion, that great care must be taken to avoid excess electrolyte or caustic, as these grain out the soap and the ideal state for this stage, the oil-in-water emulsion, can be destroyed.[14]

[12] J. W. McBain, in *Advances in Colloid Science*, Vol. I, Interscience, New York, p. 124.

[13] E. L. Smith, *J. Soc. Chem. Ind.*, *51*, 337T (1932) ; and *Soap*. 8, No. 12, 59 (1932).

[14] E. J. Better, *Seifensieder Ztg.*, *61*, 145 (1934).

With the cold process there is at the beginning a large excess of caustic alkali present, which must salt out the soap completely, and it is known that soap in this state tends to promote the formation of inverted or water-in-oil emulsions.

When a cod liver oil soap solution is salted out in the cold with a large excess of soda, the soap appears as finely granular particles of curd. If the temperature is raised the curd particles soften, conglomerate, and become gelatinous. The more concentrated the alkali, the higher the temperature at which this effect occurs. The softening undoubtedly indicates the transformation of some of the soap present to the anisotropic gel phase, neat soap
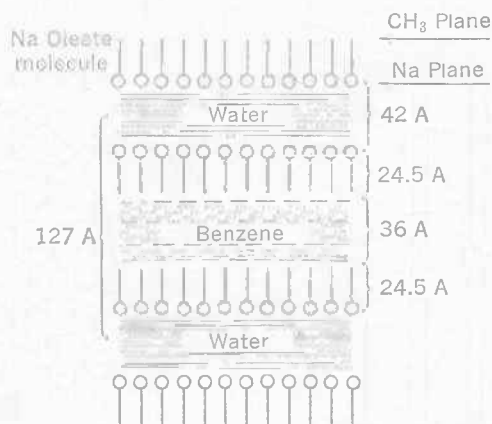
Fig. II-3. Schematic diagram of a micelle in a system in which 100 grams of an aqueous solution of 9.12 grams of sodium oleate solubilized 72 grams of benzene (0.791 gram benzene per gram oleate).[12]

(see Ch. IV, Sect. 4). When excess oil is present, moreover, there is evidence that the soap dissolves or absorbs a considerable proportion of oil, which tends to soften the curd–neat mixture.

Throughout these cold process experiments, the course of reaction was characterized by a marked period of induction, followed by a rapid increase in rate to an almost constant value showing little diminution up to 80 to 90% of the reaction, after which the reaction rate decreased as the reaction approached completion. Such behavior is characteristic of an autocatalytic reaction and has been noticed previously, in studies on the saponification of oils, both by the cold process and by the soap boiling process. The special significance of the study of E. L. Smith, however, was to be found in the fact that the reaction pursued the same course when the saponification mixture was left entirely at rest and at constant temperature after the preliminary emulsification.

This study of the mechanism of the saponification led to the following conclusion. There is evidence that both oil and alkali are soluble in soap in the form in which it occurs in cold saponification mixtures. Since there is also evidence that the soap is situated at the oil-alkali interface, and therefore in intimate contact with both phases, there is every likelihood that the soap will serve as the reaction medium. This would account satisfactorily for the velocity of saponification increasing continuously up to about half-reaction. The reaction is autocatalytic because the reaction medium (soap), is itself a product of the reaction. As more is formed, a greater proportion of the oil and alkali can be dissolved and react in a given time. A stage must occur, however, when sufficient soap has been formed to dissolve all the remaining oil, and from this point on the reaction rate must decrease. From what is known of the solubility of oils in soap, this would be expected to occur just after 50% of the reaction has been completed, a fact confirmed by experiment. It must further be concluded that the concentration of alkali in the soap is practically independent of the alkali concentration in the lye with which it is in contact, since experiment has shown that the saponification rate, within limits, is independent of alkali concentration. The curd or neat soap in which alkali and fat are dissolved can be regarded altogether as a single phase and if this is so, the saponification reaction can be considered as a homogeneous reaction, contrary to the previous view which held it to be heterogenous.

The actual circumstances in which the saponification reaction occurs, whether *in* the soap micelle according to what seems to be Smith's conception, *or on the surface* of the micelle, are not yet known. In McBain's opinion,[10] E. L. Smith's explanation of solubilization has been repeatedly misquoted in recent years. His real conception of solubilization actually described by him on several occasions implies that the organic solute (in our case the free fat) is adsorbed *on* the colloidal soap particles.

Lascaray, on the other hand, denies that the saponification, even during the rapid stage, could be regarded as a homogeneous reaction and he is of the opinion that the dissolved fat has first to reach the surface of the micelle by diffusion from the inside before meeting the alkali there.

It must be mentioned that, according to Smith's investigation, saponification velocities were generally higher with caustic potash than with caustic soda and that the reason for this, in his view, lay in the different natures of the respective soaps. Potash soaps are more soluble and tend to salt out to a lesser degree.

Applying the results of Smith's experiments on the cold process to the soap boiling process, the following conclusions may be drawn.

In the soap boiling process the phases normally present are oil, concentrated lye, neat soap, and curd soap. The saponification proceeds best when

the neat soap predominates over the curd. In the boiling process the concentration of alkali and salt in the pan are usually kept carefully adjusted so that the soap is salted out as neat soap. Too small a concentration causes the soap to pass into viscous isotropic solution, a condition called bunching, which is very much feared and avoided by the practical soapmaker. Too great a concentration of electrolyte is also avoided because the soap is salted out to a curd, and the rate of saponification consequently decreases. The boiling process seems to be quite similar to the cold process in all essential factors with the exception that the lye is more dilute and the neat soap phase tends to be less viscous owing to the higher temperature. Neat soap may absorb as much as its own weight of oil. (For definitions of the the terms neat soap, curd soap, and other soap phases, see Chapter IV, Section 4.)

The concept of the saponification of oil by aqueous alkali as an exclusively interfacial reaction is untenable in many cases. In industrial soapmaking, both by the cold process and by the soap-boiling process, the soap formed is mostly salted out to neat soap (or curd soap), which serves as the medium in which saponification proceeds. Reaction at the interface (in emulsion) is of great importance only during the early stages of saponification, in which no soap is present initially and soap is only slowly formed in preparation for the subsequent stages of the saponification.

Summarizing the main results of his experiments, Smith enumerates the following facts.

(i) The saponification reaction proceeds autocatalytically even at rest and at constant temperature.

(ii) The saponification velocity is independent of the concentration and excess of alkali used except during the induction period and within certain limits.

(iii) Caustic potash saponifies oils and fats much more quickly than caustic soda.

(iv) The soap boiling process can be accelerated considerably by the addition of soap or to a lesser extent by the addition of oil.

For all these facts, only the theory of an homogeneous reaction is able to give a satisfactory explanation.

(D) THE PHASE OF SLOW SAPONIFICATION

During the fast stage the velocity of saponification increased at the rate at which soap micelles were formed. However, it was stated that, as soon as the quantity of soap produced became sufficient to dissolve the rest of the available oil, the reaction tended to slow down. This can be understood easily when we consider a soap micelle as the medium in which the saponification occurs. According to the law of mass action a reaction must slow down when the quantity of one or more of the reactants is reduced. It is obvious that this must be the case when the fat available for solution in the micelle is at a minimum.

The normal saponification reaction can be practically conducted to total completion. It was believed in the past that, due to the hydrolytic splitting of soap by water into free alkali and fatty acid, the saponification reaction cannot be pushed beyond a certain limit. This is a misconception, since hydrolysis counteracts only the neutralization of fatty acids by alkali. It must also be considered that, in the concentrations occurring in the final stages of soap boiling, hydrolysis takes place only to a minor extent. Exact investigations carried out recently on soap solutions in such concentrations have confirmed these conclusions. The splitting of the last traces of neutral oil into fatty acids and glycerine proceeds unhampered under the influence of the splitting action of the concentrated soap solution. Soap produced by the interaction of exactly equivalent quantities of fat and alkali would, at the point of completion, contain minute traces of free fatty acids and an equivalent quantity of free alkali. In practice, however, boiled soap is always made by using a small excess of alkali at the end of the operation.

Great care was taken in the past to reduce the remaining unsaponified fat in the soap to a minimum and it was advocated by practical soapmakers that the saponification process should always be concluded by a special "strong change." This strong change was carried so far by some soapmakers that the boiling was performed in a quite "open state." This meant that caustic soda was added in such quantities that the soap was grained out partially or even totally. It is known, however, that, at this stage of the reaction, fat can be saponified much better and more quickly when the condition of the soap is "closed." The last stages of saponification call for a highly concentrated, viscous condition of the soap in which only minimum quantities of electrolytes (caustic and salt) are present.

Davidsohn[15] called attention to the fact that, when using the cold process, complete saponification can be obtained easily and within comparatively short periods of time. It is obvious that the conditions prevailing at the end of cold saponification, as will be seen later, answer very well to the above-mentioned requirements.

(6) General Rules Derived from Kinetic Studies of Saponification

(A) BOILING CONDITIONS

In order to draw some practical conclusions from the foregoing discussion, let us consider now the optimum proportions in which fat, alkali, and water should be present during the various stages of soap boiling.

In order to bring about emulsification and to promote saponification, the caustic soda concentration should be adjusted to remain somewhat below the point at which the soap produced is salted out. This concentration is termed

[15] J. Davidsohn, *Seifensieder Ztg., 1927,* No. 15.

the "lye limit concentration" and is defined as the concentration of the aque-
ous electrolyte solution in which the soap cannot be dissolved further. The
figures expressing these concentrations are data characteristic for each fat.
Thus tallow soap is salted out completely from a solution containing 5.1%
of caustic soda or 5.4% of salt, whereas coconut oil soap is salted out only
when the concentrations of caustic soda and salt reach 19.6 and 24.0%, re-
spectively. Consequently, a fat mixture containing tallow and coconut oil
may be treated from the beginning with more concentrated lyes than tallow
alone, without running the risk of destroying the emulsion.

At this stage, and almost to the end of saponification, great care should
be exercised by the operator to see that at no period is the mass allowed to
remain without at least a slight excess of alkali or a certain minimum concen-
tration of electrolyte. It will be remembered that the experiments of Smith
revealed the extent to which the addition of fat to the saponification mixture
is able to increase the rate of saponification. It is obvious that whenever
such a sudden increase in the rate of splitting of the neutral fat is caused by
the presence of a fat surplus in the kettle, the absence of an equivalent sur-
plus of alkali will cause the splitting reaction to overtake the process of neu-
tralization, which may lead to the formation of the so-called acid soaps—ad-
dition compounds between neutral soap and free fatty acids. Acid soaps
form dense and viscous masses in the soap kettle—a characteristic occurrence
for the condition known as "bunching." There is, however, another explana-
tion for bunching derived from the concept of the existence of different
"phases" in which soap may occur. These phases (Ch. IV, Sect. 4) are only
dependent on electrolyte and soap concentrations in the watery solution.

According to McBain and Langdon,[16] the dense and viscous soap in the
kettle when bunching occurs is identical with "middle soap," which has been
recognized by these authors as one of the phases in which soap may appear
at low electrolyte concentrations. Ferguson and Richardson[17] found that
tallow soap solutions at the concentration of 26 to 60% anhydrous soap will
be transformed into a similar phase as observed with the condition of bunch-
ing whenever the electrolyte concentration falls below the limit of 1%.
With coconut oil soap there is a danger limit at quite a different range, e.g.,
40 to 68% of anhydrous soap, but up to 3% of salt.

It is obvious that the failure to keep the electrolyte concentrations above
the dangerous minimum by adding sufficient amounts of caustic or salt may
constitute the cause for bunching. Great care should be taken that, when-
ever it becomes necessary to add water during saponification, it should be
done in conjunction with very thorough agitation by mechanical means or

16 J. W. McBain and G. M. Langdon, *J. Chem. Soc. London*, *127*, 852 (1925).
17 R. H. Ferguson and A. S. Richardson, *Ind. Eng. Chem.*, *24*, 1329 (1932).

by vigorous boiling with steam. Otherwise, the water may locally dilute the electrolyte and cause bunching.

Another precaution against bunching is used by most practical soapmakers when they add certain amounts of salt or soda ash to the caustic solution. Thus, it is known that in the boiling of soft soaps from linseed oil with caustic potash the caustic solution must always contain an addition of potassium chloride or potassium carbonate. Such additions constitute safe practice, since even when the caustic actually happens to be exhausted in the kettle sufficient electrolyte will remain present to keep the boil at the proper condition to prevent bunching.

During the autocatalytic or quick saponification stage, the caustic concentration should be kept at such strength as to promote the formation of neat soap, but, as pointed out by Smith, a higher concentration than necessary will not increase the rate of reaction.

(B) The Strengthening Change (or Strong Change)

As to the last phase of the saponification it is known that it is regarded as the most critical of the three, for it is at this stage that the soapmaker must make sure that no considerable portion of unsaponified fat remains in the soap. It is considered dangerous for the keeping qualities of the soap when it contains more than 0.1% of unsaponified fat. Insofar as the plan to be followed for the thorough elimination of unsaponified fat from the soap, essentially two schools of thought exist.

Davidsohn,[18] in describing the European practice of soap boiling, has pointed out that the best way to obtain complete saponification consists in leaving the viscous soap mass standing over the night shift, first making certain that it does not contain a larger amount of electrolytes than about 0.4 to 0.5% free caustic soda. However, this requirement is undoubtedly quite difficult to maintain, especially when the graining-out operation is accomplished by using salt exclusively, as has been common practice in Europe. The analysis of many samples of European commercial base soaps at that time (1929) showed almost invariably up to 0.8% unsaponified fat. The American practice of soap boiling is characterized by using, whenever possible, caustic soda (instead of salt) for graining, by boiling with alkaline liquor, and by finishing (or fitting) the closed alkaline mass by separating it with salt. Since American products generally had better keeping qualities, Davidsohn recommended the American method and the traditional conditions of the "strengthening change."

Another discussion of the merits of the two methods was published by Kawakami,[19] who carried out detailed investigations to find the most suitable

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[18] J. Davidsohn, *Seifensieder Ztg.*, 65, 293, 303 (1929).
[19] Y. Kawakami, *J. Soc. Chem. Ind. Japan*, Suppl. p. 263B (1931).

concentration of alkali as well as the length of boiling period required in
order to ensure the most complete possible saponification during the strength-
ening change.   The experimental results are reproduced in Figs. II-4 and
II-5.[19]   The points marked by plain dots are data from experiments carried
out on the heterogeneous system neat soap–lye, which corresponds, according
to J. W. McBain and Y. Kawakami,[20] to the pan condition at which the most
rapid final saponification takes place.   Points marked with circles represent
values obtained by the European method described by Davidsohn and accord-
ing to which the pan contains 50% soap and 0.4 to 0.5% free caustic at
optimum conditions.
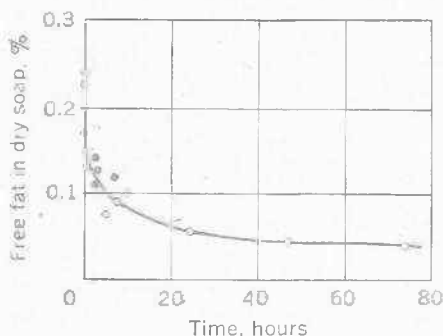
Fig. II-4.   Effect of the strengthening
change.[19]
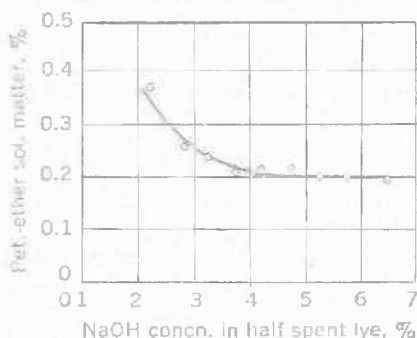
Fig. II-5.   Caustic soda concentration
in the lye vs. unsaponified fat.[19]

Kawakami shows by the results of 80 practical experiments on the
strengthening change operation that the caustic concentration of the half-spent
lye must be at least 3% for thorough saponification, from which he concludes
that boiling during the strengthening change, with its higher alkali concen-
tration, is somewhat superior to the less alkaline condition advocated by
Davidsohn.   In the above-mentioned experiments the alkali concentration
of the half-spent lye was varied while the total equivalent electrolyte concen-
tration was kept at a constant value of 11%.   The unsaponified fat was deter-
mined and recorded after two days of boiling in the heterogeneous condition.

The authors recommend as the most proper strengthening change the
following procedure, which seems to constitute probably the best compromise
of European and American soap boiling methods.

After the last salt wash, the spent lye is drawn off.   Some water is added
to the grained soap and the pan content is brought to a closed state and
boiled thoroughly with steam for four to six hours, keeping the concentration
of alkali constant to 0.4 to 0.5%.   The pan content is then grained-out by
concentrated caustic solution and boiled again with the alkaline liquor in

[20] J. W. McBain and Y. Kawakami, *J. Phys. Chem., 34,* 580 (1930).

this grained-out condition for another four to six hours in order to obtain the utmost degree of saponification.

It will be seen in later chapters dealing with the description of the practical soap-boiling process that many modern experts apparently believe that the use of a special strong change is superfluous; in fact, some go as far as to regard it to be obsolete and unnecessary.

(□) How to Control Proper Boiling Conditions

We have already touched upon this problem and stated that by providing the proper proportions of electrolytes the boil can be kept at the optimum viscosity conditions. This is especially important whenever it is intended to finish and saponify the last traces of oil while the soap is in a closed condition, as advocated by Davidsohn. In this circumstance (50% fatty acid and 0.4–0.5% free caustic soda), however, the soap mass would tend to become far too viscous to be considered in the proper boiling condition. Consequently, the appropriate amount of salt should be added at this point. Actually there is always a certain amount of salt present in the pan originating from the salted-out niger of the previous boil on which the new boil was prepared.

In order to understand the way in which the electrolyte content regulates the physical condition of the boil it is of interest to study the change in viscosity of soap solutions upon addition of electrolytes. Such a study was carried out by McBain, Willavoys, and Heighington[21] and the result of their investigation is reproduced in Fig. II-6.

It can be seen that the viscosity of a soap solution increases with the addition of salt and that, quite soon, a maximum is reached. With further addition, however, viscosity drops rapidly. It is obvious that one cannot go on adding salt without reaching a concentration at which the soap is grained out from its solution. The diagram shows that the higher the soap concentration the lower is the salt concentration necessary for reaching the maximum viscosity. Somewhere below this limit concentration, viscosity reaches a minimum and the boil acquires a high fluidity. But it can be observed that a certain degree of viscosity may be attained also by keeping the salt concentration on the low side of the maximum point. This part of the curve represents a range of much lower electrolyte concentrations than those near to the limit. In this case, however, attention should be paid to the fact that in this low electrolyte range there always exists a certain tendency for bunching.

Soap, boiling in a light and fluid manner, is in all stages of the process easier to control than when the kettle contents present a heavy mass. In heavy and viscous soap steam bubbles may accumulate which could escape

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[21] J. W. McBain, H. J. Willavoys, and H. Heighington, *J. Chem. Soc. London, 129,* 2689 (1927).

easily into the atmosphere from a soap when in the proper mobile condition. The accumulating steam will, in such cases, lift the surface of the soap in the kettle and eventually boil it over. This is what happens when, by rapid progress of the saponification, the caustic soda reserve in the kettle becomes exhausted or the electrolyte content reaches the concentration necessary for maximum viscosity. Such tendency is an indication that more caustic should be added at once in order to avoid bonching.
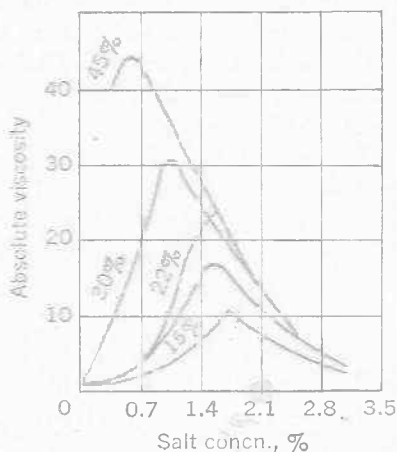
Fig. II-6. Influence of salt on the viscosity of 45, 30, 22, and 15% sodium palmitate solutions at 81° C.[21]

(7) Principles of Cold Saponification

In the course of explanations of the theoretical principles of saponification we had to refer, on several occasions, to the cold process. The cold method was used as a model reaction by many authors for the study of the saponification process in general. It will be remembered that some of the most important facts, among others the autocatalytic nature of part of the saponification process, were established by studies on the cold saponification of cod liver and coconut oils.

Cold saponification can be carried out only with concentrated caustic of 38 to 40° Bé as minimum concentration when no special conditions, such as intensive agitation or the presence of catalysts, prevail. This method was introduced as a result of the appearance of coconut and palm kernel oils as raw materials for soapmaking. Prior to the appearance of these fats on the market, soapmakers had only dealt with fats of extreme electrolyte sensibility, and as a consequence they were only acquainted with saponification methods working with diluted lyes and at boiling temperature. With the advent of

this type of fat with very high electrolyte tolerance it was soon found possible to saponify these fats with concentrated alkali. Soapmakers also found that the results with the new method were even better, when the initial stages of the saponification were carried out at about 30° C. and not at higher temperatures. We know now that not only coconut oil can be saponified with concentrated alkalies without boiling and at relatively low temperatures, but also tallow and peanut oil. In practice, any oil and fat may be successfully saponified by the cold method when certain additional conditions are fulfilled.

Cold process toilet soaps are not made commercially by saponifying the fat with the full equivalent of alkali, because coconut oil when completely saponified with caustic soda produces a soap considerably too hard and brittle in quality. Therefore, the basic formula for cold made coconut oil soap is the conventional one, using 100 kg. of coconut oil to 50 kg. of caustic soda at 38° Bé. It will be seen later that completely saponified cold process soaps are also produced in certain circumstances and that this kind of saponification even became the basis for several "rapid" and "complete" saponification methods.

The technics of the cold saponification method will be discussed in full in Chapter XIX, Section 4. At this point, it should only be mentioned that it is generally 6 to 7 hours after the components have been mixed together that the mass becomes gradually transparent and a sample dissolved in water does not show any turbidity, which is taken as a proof of the soap having been finished.

Davidsohn and Better[22] investigated the velocity of normal cold saponification by measuring the amount of caustic soda which remained free after varying periods of saponification. In one series, coconut oil was saponified with an insufficient quantity of caustic soda; while in another series, the stoichiometrically equivalent quantity of alkali was used, but in such a way that 30% of the fat was ultimately saponified with caustic potash and the remainder with soda. Fig. II-7 represents typical results from the first series of experiments.

The results show clearly that the alkali reacts at once with the free fatty acids present, but they prove also that no further soap formation takes place during the first 90 minutes, that is, within the period during which the fat-alkali mixture was continuously emulsified by agitation. During this period the viscosity of the mass increases considerably and at a much higher rate than observed after the first few minutes of soap formation. As no soap is produced during this period, gradual soap formation as a cause for the change in viscosity must be ruled out and the conclusion reached that the increase

22 J. Davidsohn and E. J. Better, *Fettchem. Umschau, 40,* 26, 52 (1933).

of viscosity is the result of mechanical emulsification in the presence of the emulsifier (available almost from the first moment).

In the next period, during which the bulk of the soap is formed, the rate at which the free alkali disappears represents the gradual speedup of the saponification reaction. However, close to the end, the reaction slows down again and the last traces of alkali disappear at a very slow rate.

The experiments with mixed soda-potash saponification (Fig. II-8[22]) indicated a much higher reaction rate.

In fact, this soap was ready in half of the time required for those made with caustic soda only. Cold made soap produced in accordance with the practical formula using 50 kg. of caustic soda of 38° Bé to 100 kg. of coconut
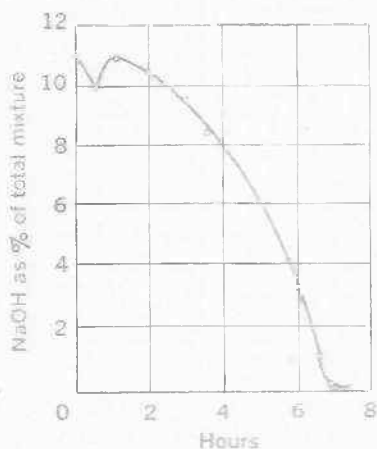
Fig. II-7. Cold saponification with   Fig. II-8. Cold saponification with
        caustic soda.[22]   caustic potash.[22]
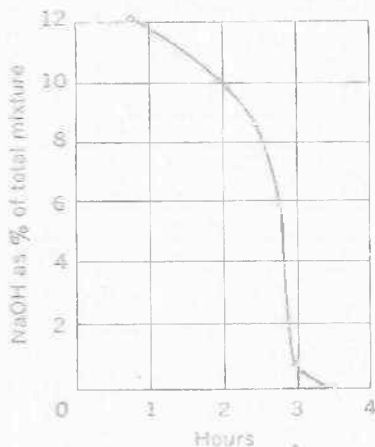
oil, should on the basis of a normal coconut oil contain about 15% of unsaponified fat. When the routine method for the determination of the unsaponified fat is employed, it usually gives a value showing no more than 3% of unsaponified fat. This method consists in extracting the unsaponified fat from a 50% alcoholic solution of the soap by petroleum ether. With another method, namely the extraction of the unsaponified fat from the previously dried soap by ethyl ether, about 12–14% fatty matter are obtained.

Under these circumstances, it must be rather surprising that a cold made soap can be dissolved at all in distilled water and that, in addition to this, it displays generally excellent keeping qualities. The phenomenon of solubility seems to prove that in the cold made soap 15% of unsaponified fat is present in a form in which it is soluble in water. Experiments of the authors demonstrated that normal coconut oil could not be dissolved in coconut oil

soap solutions and, consequently, it had to be concluded that the unsaponified fat in the cold made soap is not present in the form of ordinary neutral fat, but rather is present in the soap in the form of a mixture of mono- and diglycerides with some free low molecular fatty acids. The mono- and diglycerides of low molecular fatty acids are relatively easy to disperse in soap solutions and at the same time they are insoluble in petroleum ether. This explains the apparent contradiction between the result of the determination with petroleum ether and ethyl ether, respectively. It will be remembered that the presence of mono- and diglycerides in the partially saponified fat was regarded as a proof of the stepwise nature of fat saponification (Sect. 4B).

Making the assumption that ordinary triglycerides would produce milky emulsions when dispersed in soap solutions, while monoglycerides of lower fatty acids and to a lesser degree their diglycerides would give more or less clear dispersions, it was of interest to investigate the behavior of a series of cold made soap solutions, differing from one another only by their varying

TABLE II-1

EFFECT OF COLD SAPONIFICATION WITH VARIOUS AMOUNTS OF CAUSTIC SODA

No.	Caustic soda used as % of amt. necessary for complete saponif.	Consistency of soap	Sol. of soap in		Free NaOH, %	Unsaponified and unsaponifiable fat, ether method, %
			Dist. water	50% alc.		
1	100	Brittle	Perfect	Perfect	0.02	0.9
2	90	Less hard	"	"	0.045	3.8
3	81	Not totally solid	"	"	0.03	10.0
4	75	Quite soft	"	Solution opalescent	—	10.9
5	72	Still softer	Insoluble	Insoluble		

degrees of saponification. It was of especial interest to establish the minimum quantity of caustic soda for the saponification which would produce a soap clearly soluble in distilled water. Table II-1 presents the experiments establishing these facts.

The already mentioned cold saponification experiments of E. L. Smith were carried out under different conditions. He considered that more useful information regarding the mechanism of the saponification reaction could be obtained by working at a constant temperature than by allowing the heat of reaction to change the temperature of the mixture, as in industrial practice. His apparatus consisted of a flat-bottomed glass tube closed by a one-hole rubber stopper, through which a metal rod was inserted attached at the lower end to a perforated disk fitting loosely in the tube. About 15 to 20 g. of oil was saponified, keeping the temperature constant by agitating with the perforated disk and plunger. The degree of saponification was calculated in

the experiments of Smith by treating a sample of soap fat mixture with mineral acid and liberating the fatty acids from the soap. In this way, a mixture of free fatty acids with neutral oil was obtained in which the free fatty acid content was determined by titration. The proportion of free fatty acids in the mixture was taken as a measure of the progress of saponification.

The main facts established by these experiments are as follows:

(a) Until the reaction is about 30% complete it is possible to increase the rate of saponification by vigorous agitation; however, beyond this point the velocity is entirely independent of particle size.

(b) After the reaction is 30% complete, it is autocatalytic and the rate increases very rapidly until 50% completion, after which the rate continues to increase somewhat less rapidly.

(c) After about 90% completion, there is a definite drop in rate.

(d) The rate of saponification is independent of alkali concentration, but can be increased by addition of soap or fat.

(e) The saponification velocity is much higher with caustic potash than with caustic soda.

The results and conclusions of Smith have already been discussed (Sect. 5C), and the following discussion will point out the differences existing between the boiling and the cold processes.

The emulsion in the cold process is initially a water-in-oil type, while that in the boiling process is essentially an oil-in-water type. In cold saponification, the alkali solution is concentrated to such an extent that the soap is practically in a salted-out condition. When in this state, soap promotes and stabilizes water-in-oil emulsions, while in dilute solution it produces oil-in-water emulsions. As more soap in the neat phase is formed, the soap takes on a new role in addition to that of an emulsifier. In this new phase the soap in its micellar condition serves as an autocatalyst. Thus, it will be seen that the cold saponification process and the boiling method differ, in principle, only in the first phase, while the later phases may be regarded as almost identical.

It may sound strange, that, depending on conditions, soap should be able to serve both as an oil-in-water and as a water-in-oil emulsifier. The soap molecule contains a paraffin group ($CH_3CH_2CH_2$—) and a carboxyl group to which the sodium or potassium atom is attached. The two different parts of the soap molecule display completely contrasting properties. The paraffin chain is hydrophobic, while the carboxyl pole is strongly hydrophilic. As a result of this "polar" property of the soap molecule the paraffin chain will tend to withdraw from the water and to remain at the surface outside the solution. The carboxyl pole opposes this tendency, so that the molecule will finally orient itself in a perpendicular position at the surface of the solution with the carboxyl head dipped into the solution and the paraffinic tail protruding.

In emulsions, when small oil droplets are finely dispersed in water as in milk, or, conversely, when fine water droplets are dispersed in a medium of oil as in butter, we have examples of the oil-in-water or the water-in-oil type, respectively. In all emulsions one phase will always appear in the form of fine droplets dispersed in the other, or continuous, phase.

Whenever soap serves as emulsifier at the interface, there will always be a molecular layer of soap molecules arranged in parallel, the carboxyl heads of which will always be dipped into the water and the paraffin chain pointing in the direction of the oil.

As already explained, alkali soaps preferentially stabilize oil-in-water emulsions, but metallic soaps like lime or magnesia soaps stabilize water-in-oil emulsions. However, it has been found that soap in relatively water-free condition behaves as a hydrophobic substance, and therefore stabilizes water-in-oil emulsions in these circumstances. In the cold saponification process, as a result of the high alkali concentration prevailing, the soap particles at the interface are practically salted out and dehydrated. In this dehydrated state they cause the water to disperse in small droplets in the oil. Soap in diluted alkali lyes, on the other hand as prevails in the boiling process, would behave as a hydrophilic substance and cause the oil to be dispersed in the form of minute droplets within the water.

It is comparatively easy to determine which of the two emulsion systems prevails. In the case of water-in-oil emulsion, it is the oil which forms the continuous phase; in the case of oil-in-water emulsions it is the water which forms the continuous phase. In order to establish which constitutes the continuous phase, we have only to add an oil-soluble dye to a drop of the emulsion. For the water-in-oil system it will be the continuous fluid surrounding the dispersed droplets which will be colored by the dye, and this is taken as evidence that the emulsion belongs, in fact, to the above type. The same experiment can be carried out with a water-soluble dye, and the results must then be interpreted accordingly.

As mentioned earlier, cold saponification gives quick and complete results also with charges containing other fats than coconut oil. J. Davidsohn was the first to recommend this method as the easiest and quickest way to achieve complete saponification in industrial practice, with any kind of fat charge. One of the so-called rapid saponification processes is based upon this basic principle.

Another modification of the cold process is incorporated in U. S. Patent 1,831,610, which states that it is possible to bring about very rapid saponification by the simple kneading of 40.7 parts of dry caustic soda powder into a mixture of 300 parts of corn oil, with 16.3 parts of water at 40–70° C. After a few minutes of this treatment, the resulting mass is dropped into a form, where the reaction heat raises the temperature of the mixture very

rapidly to 150° C. Consequently, water is evaporated and the mass becomes inflated by gases. After 8 to 10 minutes the mass breaks down again and saponification is complete in another 25 to 30 minutes. The result is a soap containing no more than 7.2% water. Davidsohn and Krings were able to confirm that it is possible to produce soap by this method on a practical scale.

(8) Catalysts in Saponification

The following cold saponification experiments were performed by Roshdestwensky.[23] Coconut, cottonseed and linseed oils were saponified by the cold process in the presence of 1% solutions of α-naphthol, β-naphthol, cresol, and thymol. The unsaponified fat was determined periodically by the petroleum ether extraction method. Table II-2 shows the result of these ex-

TABLE II-2

CATALYTIC INFLUENCE OF CHEMICALS ON THE RATE OF SAPONIFICATION[23]

Catalyst	Oil (%) reacted after								
	minutes			hours					
	20	40	60	2	3	4	24	70	76
Coconut oil	—	—	13.5	24	—	94	—	—	—
+1% α-naphthol	95	100	—	—	—	—	—	—	—
+1% β-naphthol	92	100	—	—	—	—	—	—	—
+1% cresol	90	94	—	—	—	—	—	—	—
Cottonseed oil	—	—	—	—	7	—	42	100	—
+1% α-naphthol	—	100	—	—	—	—	—	—	—
+1% β-naphthol	—	98	—	—	—	—	—	—	—
+1% thymol	—	92	98	—	—	—	—	—	—
Linseed oil	—	—	—	—	6.2	—	37	—	100
+1% β-naphthol	82	100	—	—	—	—	—	—	—

periments. It is observed that it is much more difficult to saponify unsaturated oils than saturated ones, and that certain phenolic substances greatly increase the saponification velocity of all of these oils and fats.

Smith reports that very high reaction rates can be observed when oxidized fats are being saponified. This phenomenon was confirmed by Better with sesame seed oil.

Oxidized oils are stabilizers for water-in-oil emulsions, and are widely used for that purpose in the margarine industry. It is possible that these saponification catalysts act as stabilizers in the water-in-oil system and shorten or completely eliminate in this way the first slow period of saponification.

The knowledge of substances which are able to increase the rate of saponification by catalytic action is very important for the practical soapmaker, as

[23] D. Roshdestwensky, *Seifensieder Ztg.*, *55*, 116, 127 (1928).

in many cases, for instance in perfume compositions used in cold made soaps, compounds may be present which are able to act as saponification catalysts. E. J. Better and A. Davidsohn found that certain perfume compositions containing amyl and benzyl salicylates actually act as saponification catalysts. Better[24] also found that origanum oil has very great catalytic activity which he attributes to the presence of carvacrol (a phenolic compound homologous to thymol) in this essential oil. Table II-3 presents the constitutional formulas of a few catalysts mentioned in the literature, in addition to those discovered by Better and Davidsohn.[25]

The experiments of Better and Davidsohn were carried out by preparing cold made soaps from coconut oil in the usual way, but dissolving 0.2% of the sample in the oil before the lye was mixed with it. The time spent mixing the components until the emulsion thickened was recorded and taken as a measure of the catalytic activity of the compound. Substances which did not cause the emulsion to become viscous within ten minutes were not regarded to be active. Such substances were, for instance, hydroquinone, resorcinol, benzoic acid, benzaldehyde, benzyl alcohol, and salicylic acid.

The following general conclusions may be drawn from these experiments:

(a)   The only substances found to be active were those in which one —OH group is directly bound to an aromatic ring.

(b) Aromatic monohydroxy compounds containing side chains are more active than those without such chains.

(c) Aromatic di- or polyhydroxy compounds, or monohydroxy compounds containing a carboxylic group, are inactive.

(d) When the carboxylic group is esterified, the compound again becomes active.

(e) An aromatic dihydroxy compound also becomes active when the second —OH group is etherified.

(f) The introduction of a carbonyl (aldehyde) group into a monophenol increases the activity, but such compounds are less active than those with a paraffin side chain.

(9) Saponification under Pressure and at Temperatures Higher than 100° C.
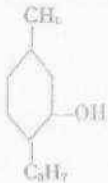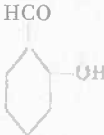
Saponification under pressure and at temperatures in excess of 100° C. is the basis for various modern continuous soap-manufacturing processes. These processes will be discussed in detail in a later chapter, and only fundamental data and older experiments will be treated here.

As already mentioned the studies of McBain and Norris made it clear that

[24] Unpublished experiments.
[25] Unpublished experiments.

TABLE II-3

CATALYTIC INFLUENCE OF CHEMICALS ON SAPONIFICATION[25]

Compound:	α-Naphthol	β-Naphthol	Cresol	Thymol
Formula:	OH (structure)	OH (structure)	OH / CH₃ (structure)	CH₃ / OH / C₃H₇ (structure)
Seconds:	?	60	25	45

Compound:	Carvacrol (origanum)	Amyl and benzyl salicylates		
Formula:	CH₃ —OH C₃H₇ (structure)	COOCH₂C₆H₅ —OH / COOC₅H₁₁ —OH (structures)		
Seconds:	60	45		

Compound:	Phenol	Salicyl aldehyde	Hydroquinone monomethyl ether	
Formula:	OH (structure)	HCO —OH (structure)	OH / OCH₃ (structure)	
Seconds:	400	160	90	

with normal saponification the average temperature rate coefficient is not more than 1.5, which means that by raising the temperature of the saponification mixture by 10° C. the increase in the rate of saponification is only 1.5 times the velocity it was before the temperature change. The same workers found that four hours are required for the complete saponification of soybean oil by intensive stirring with the equivalent quantity of a 4% caustic soda solution at 100° C.

Mattikow[26] calculated the theoretical saponification time for various temperatures above 100° C., based on the assumption that the reaction follows a bimolecular course, as explained on Sect. 4A.   It is seen from Table II-4

TABLE II-4

SAPONIFICATION VELOCITY AT HIGH TEMPERATURES AND HIGH PRESSURES[26]

Saponif. temp.		Total saponif. time			Pressure of satd. steam to which temp. corresponds	
°F.	°C.	Hrs.	Min.	Sec.	P.s.i.	Atmospheres
212	100	4	—	—	14.69	1
230	110	2.66	—	—	20.77	1.46
248	120	1.77	—	—	28.79	2.02
266	130	1.18	—	—	39.17	2.75
284	140	—	47	—	52.39	3.68
302	150	—	31	—	69.01	4.85
320	160	—	21	—	89.59	6.30
338	170	—	14	—	114.79	8.07
356	180	—	9.5	—	145.30	10.21
374	190	—	6.2	—	181.85	12.78
392	200	—	4.2	—	225.23	15.83
410	210	—	2.7	—	276.34	19.42
428	220	—	1.8	—	336.24	23.63
446	230	—	1.2	—	400	27
464	240	—	—	50	500	34
482	250	—	—	33	600	41
500	260	—	—	22	700	47.5
518	270	—	—	14.7	800	54
536	280	—	—	9.6	900	61
554	290	—	—	6.5	1100	75
572	300	—	—	4.3	1250	82

that at pressures below 2.5 atmospheres one hour is required for complete saponification; below 10 atmospheres only ten minutes are required, and at about 80 atmospheres the reaction is finished in four seconds.   Mattikow points out, however, that at this last very high temperature and pressure the reaction undoubtedly becomes homogeneous, and the temperature rate coefficient reaches the value 2 established as a general rule for homogeneous reactions (van't Hoff).   With this assumption, calculation of reaction time gives a value of 0.00306 second at 290° C.; the reaction thus has to be considered to be practically instantaneous at this temperature.

Many small- and large-scale experiments were performed in the past to find a practical method for obtaining the quick and total saponification which results from using high-pressure and high-temperature apparatus.   There

[26] M. Mattikow, *Oil and Soap*, *17*, 184 (1940).

have been long and lively discussions about the practical value of the methods by which fats are saponified in pressure vessels in batch processes. The opinion of manufacturing experts seems to have been negative on the whole, and pressure saponification in batch processes did not succeed in gaining any popularity. It was recognized that under conditions prevailing in the average soap plant, where generally only steam up to 6 atmospheres is available, the increase in the saponification rate is not really such as to make the pressure process attractive enough. On the other hand, it was often pointed out that dangers are inherent in such a process, since it happened, for instance, that saponification failed to start normally and then with the sudden buildup of the reaction so much heat and pressure were generated that the vessel exploded. It is known that, because of this danger, pressure saponification processes in batch systems were abandoned in some well-known plants where they had already been introduced on an experimental scale.

In this connection, the following thermal calculation should be noted. Suppose 1000 kg. of fat is to be saponified in a closed vessel and at a given moment 800 kg. of the charge suddenly enters into the reaction. 1 kg. of fat generates 52 Cal. (according to the calculation given in Sect. 3). If we assume that the soap contains 50% fat in the vessel, or a total mass of 1800 kg., and also that the specific heat of the soap mass is 0.65, then the sudden temperature rise will amount to

$$\frac{41,600}{1800 \times 0.65} = 36^\circ \text{ C. (Lascaray[1])}$$

It is true, on the other hand, that the pressure procedure offers considerable economic advantages—mainly by permitting the whole process to be shortened and economizing on the quantities of steam required for long hours of boiling. In addition, it was found to be possible to use the generated heat for subsequent operations, and in one patented process, at least, the soap was sprayed directly into a spray chamber utilizing the pressure of the saponification vessel and with the temperature attained there.

However, there was another reason why certain fats were autoclaved or pressure saponified in the past. It is known that unsaturated fats can be saturated by introduction of water into the unsaturated bonds of the olefin chain. Structurally, this occurs according to the formula:

$$-H_2C-CH = CH-CH_2- + HOH \rightarrow -H_2C-HCOH-CH_2-CH-$$

This reaction takes place only under relatively high pressure, and in the presence of at least small amounts of alkali. This is why pressure saponification would not only influence the rate of saponification, but eventually also change the chemical structure of the fat under treatment. To quote an example, linoleic acid with an iodine value of 174 was treated with 40° Bé caustic soda, and the soap was then heated in an autoclave at 270° C. for three hours. The iodine value of the resulting product was only 83.4. It is not known, of course, how far this result was influenced by polymerization, but it is estab-

lished, at any rate, that fats treated in this way always produce soaps with better foaming properties and better consistencies than untreated ones.

Such saturation reactions were studied by Stiepel,[27] who tried to transform the unsaturated fatty acids of whale oil into soaps by treating them in an autoclave under various conditions. Stiepel's experiments are reproduced in Table II-5. The figures give sufficient evidence of what is happening when

TABLE II-5

SOAP FROM WHALE OIL AUTOCLAVED AND SATURATED[27]

Autoclaving conditions			Soap before treatment		Soap after treatment	
Time, hrs.	Temp., °C.	Pressure, atm.	FA, %	I.V.	FA, %	I.V.
6	200	16	40	118.6	40	98.1
6	200	16	58.5	118.6	57.9	95.6
6	200	16	67.5	118.6	68	99.4
6	200	16	74.1	118.6	73.3	99.5
6	200	16	82.3	118.6	82.1	102.5
6	250	40	58.5	118.6	59	80.6
6	250	40	67.5	118.6	68.3	82.7
6	250	40	74.1	118.6	72.2	82.5
6	250	40	82.3	118.6	82.1	84.4
3	200	16	58.5	118.6	58.5	105.8
3	200	16	74.1	118.6	71.7	106.4
3	250	40	58.5	118.6	58.2	89.5
3	250	40	74.1	118.6	73.8	89.2

unsaturated oils are saponified and subjected to high presures for some period of time. In one instance, there is a drop of 38 units of iodine value when a whale oil soap solution with 58.5% fatty acid was subjected to a pressure of 40 atmospheres. According to Stiepel's report, the resulting soap had no fish odor whatsoever, which shows that the clupanodonic acid responsible for this odor was successfully converted to some other product, possibly by saturation or polymerization or both.

There is an interesting variant to this pressure treatment of soap which, however, does not represent an example of pressure saponification. Welter[28] introduces into a 350-cu. ft. steel pressure vessel (checked and commissioned for a pressure of 40 atmospheres) about 6–7000 kg. of hot, liquid neat soap produced previously from soybean oil by any of the known soapmaking processes. In addition to this, he charges the autoclave with 200–250 kg. 38° Bé caustic soda, after which the vessel is closed. He now pumps into the closed vessel, through the soap layer, saturated steam at 10 atmospheres until the

[27] C. Stiepel, in J. Davidsohn, *Lehrbuch der Seifenfabrikation*, Borntraeger, Berlin. 1928. p. 313.

[28] A. Welter, Ger. Pat. 620391.

pressure inside the vessel rises to about 40 atmospheres. The condensate is separated from the steam prior to its entering into the vessel. The contents of the vessel remain under steam pressure for 6–8 hours, while under continuous mechanical agitation. After this period, the mass is released slowly under its own pressure into another open vessel into which about 5000 kg. of palm kernel oil had been charged. The excess of caustic from the autoclave saponifies the palm kernel oil very quickly, but some unsaponified oil will still remain which will have to be saponified by one of the usual methods. The result is a soap from a mixture of soybean and palm kernel oils, which,

TABLE II-6

SAPONIFICATION TEMPERATURES MENTIONED IN PATENTS

Patent No.	Temp., °C.	Pressure, atm.
U. S. 1,153,625 (Procter & Gamble)	125	—
U. S. 2,084,446 (Lorenz & Wilson)	250-270	—
U. S. 2,096,188 (Lorenz, Brown, Sewards & Wilson)	300	—
Fr. 756,883 (Camille Deguide)	134	2
Brit. 16,746 (Haywood)	260	—
Brit. 346,389 (Hentschel)	—	3–4
Brit. 379,760 (Leffer)	125–260	2–6
U. S. 1,918,603 (Colgate-Palmolive-Peet)	250–300	140 (in spiral)
U. S. 2,019,775 ⎱ (Refining, Inc.—Clayton-Burns) U. S. 2,037,004 ⎰	400–500	10–40
U. S. 2,126,099 (Procter & Gamble—Duncan)	316	110
U. S. 2,133,666 (Procter & Gamble—Mills)	470	35
U. S. 2,178,987-8 (Refining, Inc.)	204–288	—

MELTING POINTS OF SOAP*

Kind of soap	M.p., °C.	Kind of soap	M.p., °C.
Sodium stearate	260	Sodium oleate	232–235
Sodium palmitate	270	Sodium elaidate	225-227
Sodium myristate	250	Sodium erucate	230–235
Sodium laureate	255-260	Sodium brassidate	245–248

however, shows much greater resistance to atmospheric oxidation than a soap of the same composition, but not treated under pressure. The fatty acids of the soybean oil soap before pressure treatment had an iodine value of 122, which dropped to 53 after treatment.

It is interesting to note that Welter, who originally was one of the pioneers of pressure saponification in batch kettles, later employs pressure not

* Krafft, *Berl. Berichte*, 1899, 1598. Godbole and Yoshi, *Allgem Oel- u. Fett-Ztg.*, 27, 77 (1930), found melting points as follows; sodium stearate, 255–272°; sodium palmitate, 258–267°; sodium oleate, 230–235°.

for saponification but only for bringing about other chemical changes in the fat.

During recent years, the knowledge of the conditions prevailing when soaps are produced under high pressure and temperature gained considerable and renewed importance, due to the fact that many recent developments of continuous soap-manufacturing processes deal with saponification under high pressures and temperatures. We shall treat in detail the representative new continuous processes in another chapter.

Commercial soap in its anhydrous form is considered to have a true melting point of around 250° C. and in most of the continuous procedures the inventors endeavor to keep the soap in the liquid state. In this connection the true melting points of pure anhydrous soaps are of practical interest (Table II-6).

THE STRUCTURE OF SOAP IN THE SOLID STATE AND IN SOLUTION

While studying the principles of the saponification process during its various stages, it is observed that soap may appear throughout the course of the process in different physical forms, for instance, as a hydrated or as an anhydrous phase, as a thin or as a viscous liquid or as a solid mass. In these different forms the soap constantly displays changing properties, and it is able to perform widely differing functions. For example, it can serve as an oil-in-water as well as a water-in-oil emulsifier.

Crystalline structure plays an important role in determining the properties of soap. The development of ultramicroscope and x-ray diffraction techniques and other physicochemical methods has provided the tools which enable us to establish the structure of phases encountered in soapmaking processes, and also to predict the behavior of soap under all possible conditions.

For these reasons, it is absolutely necessary for the modern student of soap manufacture to acquaint himself with the theories of the structure of soap in its various forms. He must know the way the individual soap molecule is built, how these elements aggregate into more complicated units and how these aggregations of individual soap molecules determine the "phase" in which the soap ultimately appears. The practical man operating with soap in its changing form and appearance should also know the theories dealing with the effect of variation of concentration, electrolyte, temperature, and mechanical circumstances on the structure of these soap aggregations.

(1) Structure of the Individual Fatty Acid and of Its Aggregates

A fatty acid consists of a paraffin chain of linked —CH_2 groups with a carboxyl group —COOH group situated at one extremity of the chain. Thus, to give an example, stearic acid, $C_{18}H_{?}O_{?}$, has the constitutional formula: CH_3—$(CH_2)_{16}$—COOH.

From the publications of Mueller,[29] we know that the stearic acid molecule consists of a chain lying flat in one plane in which the —CH_2 groups form a zigzag line. The zigzag pattern is ascertained by comparing the lengths of the stearic acid and palmitic acid molecules and noting that the difference between the two is 2.52 A. Since stearic acid has 17 —CH_2 groups in each molecule and palmitic acid has only 15, the observed difference in length amounts to 1.26 A. per —CH_2 group. However, it is known from the study of other types of organic compounds that the distance between two neighboring carbon atoms is 1.54 and not 1.26 A. Therefore, this discrepancy can only be explained by assuming that in fatty acids the —CH_2 groups are not linked in a straight chain, but in a zigzag structure in which the lines connecting the centers of the groups form an angle of 109° 35'. The structure of the stearic acid molecule is shown in Fig. III-1.[29]

The chain length without the carboxyl group amounts to 20.2 A., while the carboxylic group adds another 4.2 A. to the longitudinal axis; the total length of one stearic acid molecule thus becomes 24.4 A.

The stearic acid crystal unit cell represents a monoclinic prism, and the unit crystal cell was found to contain four molecules and to measure 48.84 A. in total length, and 5.546 and 7.381 A., respectively, in width and depth. The comparison of x-ray diffraction diagrams of straight-chain hydrocarbons and of fatty acids (Fig. III-2) shows that in fatty acid crystals the longitudinal axis is inclined to the base at an angle of 63° 38'. The crystal has a "layer" structure due to the arrangement of the four molecules in two groups in such a way that all —COOH groups meet in one plane while the paraffin —CH_3 tails form the outward bases. The —COOH groups in the center of the unit crystal are tied by much stronger bonds than the paraffin tails lying in the crystal bases of two neighboring crystal unit cells. A slab of solid stearic acid contains a system of such crystal unit cells, one above the other, and side by side. The forces by which the paraffin parts of the parallel inclined chains are bound together are stronger than the cohesion between the —CH_3 groups in the bases. As a consequence, a stearic acid slab can be easily broken only in one direction, which is the plane of the crystal base.

However, it is possible to cut the stearic acid slab in two ways so that either carboxyl groups or the hydrophobic —CH_3 groups occupy the cleavage plane. It will be seen later that soap has a quite similar crystalline structure

[29] A. Mueller and E. L. Lederer, *Fettchem. Umschau*, 40, 2 (1933).

$d_1 = 22.5$ A

Hydrocarbon $C_{16}H_{38}$ 3.7 A

109° 35'

2.52 A

63°38'

48.84 A

$d_1 = 20$ A

Stearic
acid

Fatty acid $C_{17}H_{35}COOH$
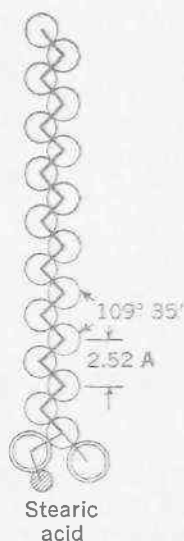
Fig. III-1.   The structure of stearic   Fig. III-2.   Hydrocarbon and fatty
acid molecules.[25]   acid crystal units.
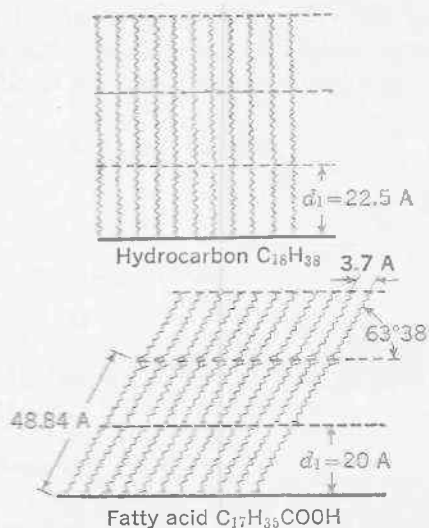
and the possibility of different cleavage planes—as schematically indicated in Fig. III-3[30]—explains why certain physical forms of the same soap might be more or less soluble in water and might possess gradually changing lathering power, depending on the conditions under which it was prepared.   Oleic acid
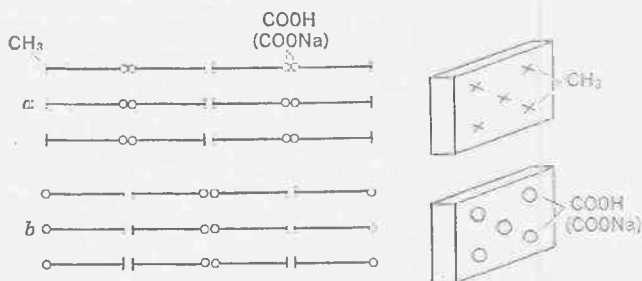
Fig. III-3.   Schematic diagram of paraffin and carboxylic
cleavage planes of a soap crystal.[30]

was found by x-ray investigation to have a shorter molecular chain than stearic acid.   Oleic acid can be transformed into elaidic acid by nitrous gases.   Elaidic acid is a solid, melting at 46°C.   It is believed that the constitutional difference between the two acids is founded in steric conditions concerning the mutual position of the pair of hydrogen atoms situated near the double linkage.

[30] P. A. Thiessen, *Angew. Chem.*, *51*, 318 (1938).

X-ray investigation has disclosed that elaidic acid possesses exactly the same chain length as saturated acids and that, accordingly, the arrangement of the chain is identical with that found in saturated fatty acids.

$$CH_3—(CH_2)_7C = C—(CH_2)_7—COOH \qquad \text{\textit{cis} form}$$
$$\qquad\qquad\quad |\ \ |\qquad\qquad\qquad\qquad \text{oleic acid}$$
$$\qquad\qquad\quad H\ \ H$$

$$\qquad\qquad\ H$$
$$\qquad\qquad\ |$$
$$CH_3—(CH_2)_7—C = C—(CH_2)_7—COOH \qquad \text{\textit{trans} form}$$
$$\qquad\qquad\qquad\quad |\qquad\qquad\qquad\qquad\qquad \text{elaidic acid}$$
$$\qquad\qquad\qquad\quad H$$
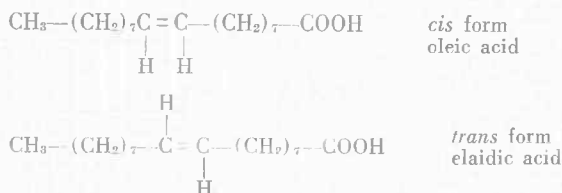
(2) Structure of the Individual Anhydrous or Slightly Hydrated Soap Molecule

Similarly to fatty acids, anhydrous soaps display all the characteristics of a crystalline body. The dimensions of the individual soap molecule are very much the same as those of the fatty acids from which they are derived. The lengths of an individual soap molecule of the kind that occurs in commercial soaps range between 18 and 25 A., depending on molecular weight and degree of saturation. While the dimensions of a soap molecule are not very much different from those of a fatty acid, the presence of the alkali atom in the carboxylic group changes the character of the molecule fundamentally. Soap is an alkali salt of a fatty acid and contact with water will result in electrolytic dissociation. The alkali ion will be positively charged, and the anion (the fatty acid balance of the molecule) will be negatively charged. The anion is a complex containing the paraffin chain and the remainder of the carboxyl group (—COO). The paraffin tail is hydrophobic; the head of the carboxyl group is hydrophilic. We already know that the length of the paraffin chain of stearic acid or of a stearic acid salt is 20.2 A., and the carboxyl group about 4.2 A. According to the known dimensions of sodium, the length of sodium salt of the stearic acid should be 26.31 A. However, x-ray investigations disclose a slightly smaller value.

With the lower fatty acids the long dimension of the hydrophobic paraffin chain becomes shorter, while the dimensions of the carboxyl group remain the same. In fact, the shorter the fatty acid, the less hydrophobic the tail becomes and consequently the more water soluble it behaves. Essentially, the tendency of the hydrophobic paraffin chain to balance the hydrophilic character of the carboxyl group is the basic function imparting soap character to the alkali salt of the higher fatty acid. This very pronounced polar tendency of the soap molecules is responsible for the fact that they are always found to be more or less oriented when in the solid state or in aqueous solution. The orientation of soap molecules in the solid state follows very much the same system (head-to-head, tail-to-tail) as described for stearic acid.

The positively charged alkali cation is bound to the negative anion by strong interionic forces which become stronger as the molecule lengthens, as shown by the lower ionization constant for the higher soaps.

Intermolecular attraction exists between the paraffin anions of neighboring molecules. These forces are of a much smaller order than the interionic forces.

X-ray evidence by Thiessen and Stauff[30] shows that forces acting on the carboxyl groups cause two molecules of soap to aggregate in the head-to-head formation. Thiessen and Stauff also were able to crystallize sodium stearate in the rhombic system from alcohol, and they found that this alpha form was transformed into the more stable monoclinic beta form upon heating to the transition point of 52°C. The beta form cannot be reversed into the alpha form by cooling. Thiessen and Stauff explained the stability of the beta form by suggesting the arrangements shown in Fig. III-4 for the two poly-morphic modifications.
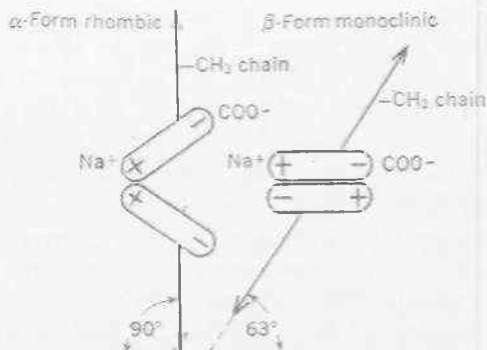
Fig. III-4. Thiessen's alpha and beta sodium stearate. In the monoclinic betaform the very stable head links of the —COOH— groups are secured by the mutual arrangement in which the positive sodium ions are situated opposite the negative carboxylic rest, and bound by strong interionic forces.[30]

Lately, more polymorphic modifications of soaps have been established (see Sect. 3) and the polymorphism of soaps attained great importance when it became apparent that the practical properties of soaps undergo fundamental changes according to the various crystalline forms in which soap may ap-pear. Up to now, four solid crystalline forms of soap are known to exist (see Section 4).

Before discussing the practical importance of these polymorphic modi-fications of soap, we have to mention another important phenomenon, dis-covered by Thiessen and Stauff, and termed by them the "genotypic transition." The melting point of soap is very high—about 250°C., compared to the melting points of the corrosponding fatty acids. Thiessen and Stauff found that when

soaps are heated above the melting point of their respective fatty acids the physical constants of the soap suddenly undergo change, indicating that transition into a new phase has taken place. This transition is, however, fully reversible and, when the temperature decreases below the transition point, the original form reappears. This genotypic point has been connected with another very important consideration. According to Thiessen, this transition point is identical with the temperature which must be exceeded when a completely clear hydrosol of the soap is to be prepared. Below this temperature the solution will start to precipitate fibery formations and develop solid white crystallization centers of various forms. It will be found later (Chapter IV, Section 5A) that this definition of the genotypic point is almost identical with the definition given by McBain and his co-workers for the value of T_c, expressing the temperature under which isotropic and anisotropic soap solutions start to form white curd fibers or vice versa.

The denomination of this kind of transition implies that the transition will take place in any kind of soap at a temperature which is characteristic for the fat composition only. This genotypic point may be obtained at quite a low temperature with fat compositions containing high proportions of liquid oils. As a rule, this transition point will be attained at or near the "titer" (the solidification point of the component fatty acids). It is quite possible that mechanical treatment at temperaures above the genotypic point may result in soap products having different properties from those normally found. It is obvious from the various kinds of rolls and plodder constructions used in soap manufacture and also from the temperature conditions that a great variety of products may be obtained. The properties of the product will depend merely upon whether the temperature during mechanical working was held above or below the genotypic transition point. This demonstrates again to what extent theoretical considerations may affect decisions belonging to mechanical technology.

According to Vold,[31] the genotypic transition loses its reversibility when the soap has been heated to a high enough temperature to reach the mesomorphic, "subwaxy," or "supercurd" form (the mesomorphic forms are discussed in detail in Chapter IV, Section 1).

In chapter IV we shall describe a hydrous soap modification that may result when soapboiler's neat soap is cooled under certain conditions. This modification is called also the "beta phase." In order to avoid confusion, Vold and Lyon[32] propose to call the anhydrous modification which results when the "alpha" form is heated *Thiessen's beta* and the other which crystallizes from soapboiler's neat soap *hydrous beta*.

[31] R. D. and M. J. Vold, in *Colloid Chemistry*, J. Alexander, ed., Vol. V, Reinhold, New York, 1944, p. 276.

[32] R. D. Vold and L. L. Lyon, *Ind. Eng. Chem.*, 37, 497 (1945).

(3) Structure of Solid Hydrated Soap Products and of Hydrosols

A cake of commercial soap has been defined[33] as "hydrated curd fibers with enmeshed liquor, which is a sol or more frequently gel of the various more soluble soaps and salts present." However, Ferguson[34] states that the fat mixture in commercial soaps seems to crystallize as a unit, and x-ray examination brings sufficient evidence to show that no fractionation of the different fatty acid salts into more or less soluble fractions seems to occur. If fractionation in accordance with the above definition takes place, this should be evidenced in x-ray diagrams, which permit the direct measurement of molecular length. Ferguson points out that when he investigated some commercial soaps by direct x-ray measurement of the molecular length the results were sufficient corroboration for the determination of the average molecular weight as found by chemical methods.
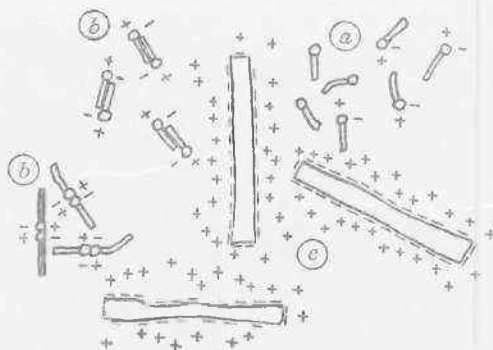
Fig. III-5.   Molecular arrangements in hydrated soaps (hydrosols).[30]

Thiessen's views[30] regarding the molecular arrangement within hydrated soap can be described as follows. Soaps appear according to their degree of hydration as hydrosols (Fig. III-5) or hydrogels (sols are the more hydrated forms of the gels). Hydrosols contain: (a) dissociated single molecules, (b) double molecules of various combinations (head-to-head, tail-to-tail), and (c) micelles which are ultramicroscopic crystals (for discussion of the interior construction of the micelles and their range of existence in aqueous solutions see Part F).

The internal molecular arrangement in the soap is governed by the orientation tendency of the soap molecule which, as already explained, is the result of its polar character. According to Thiessen and others, the double molecules as they have been described in Section 2 in their head-to-head arrange-

[33] W. F. Darke, J. W. McBain, and C. S. Salmon, *Proc. Roy. Soc. London, 98A,* 395 (1921).

ment are oriented in parallel among themselves and perpendicular to the longitudinal axis of the micelle crystal.   (See Fig. III-7.[30])

The hydrated —COONa groups are hydrolyzed and the crystal micelle thereby obtains a negative charge while the positively charged sodium or alkali
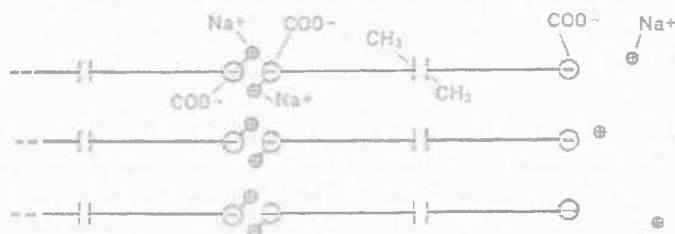
Fig. III-6.   Head-to-head arrangement of the molecules in hydrated soaps.[30]

ions envelop the micelle with a positive electric charge in the shape of what is called an "ionic cloud" or "ionic atmosphere."   (See Fig. III-6.[30])

As described, a soap hydrosol generally contains all the formations schematically demonstrated in Fig. III-5.   The proportion in which each of
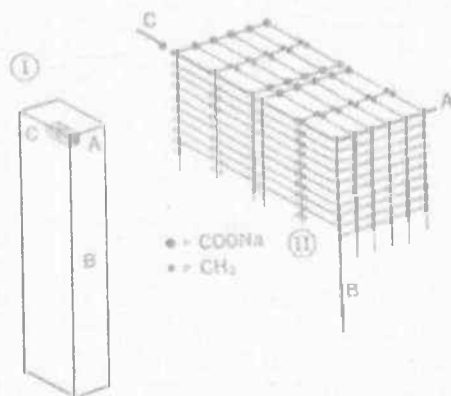
Fig. III-7.   Model of Thiessen's conception of a "micelle."   (I) is the crystalline aggregate; (II) shows the oriented arrangement in detail.[30]   The double molecules are perpendicular to the axis of length B.   The micelle is, according to the nomenclature of Thiessen, an electrically neutral formation.   But following the action of hydrolysis, the —COONa group becomes split and the micelle obtains a negative charge —it becomes an "ionic micelle."

these elements appear depends on equilibria which can be influenced by change of conditions such as the temperature and the amount of electrolyte present. Increasing soap concentration in the hydrosol or a drop in temperature increases the amount of micelles in the sol, and at the same time causes agglom-

eration of the elementary micelles. Upon slow cooling, agglomeration takes place in the direction of the longitudinal axis and produces fibers and fiber bunches (Fig. III-8), while upon rapid cooling the micelles aggregate side by side around a center and form spheric granules.
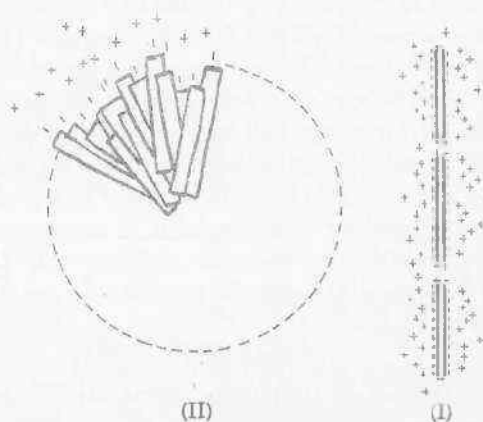
Fig. III-8. Schematic model of soap fibers (I) and of granular formation (II) in cooled soap solutions: (−) the negatively charged —COO group; (⊹) the positive sodium or potassium ion.[30]

(4) Four Known Crystalline Forms of Soap in the Hydrated Curd Phase

In 1944, Ferguson[34] wrote about this problem: "The fibers or crystals of soap may exist in distinctive modifications, with differing properties has now been established for commercial soaps of widely differing types. The first positive demonstration of polymorphism was concerned with pure single soaps (sodium palmitate and stearate) and brought to light two modifications only, the alpha and beta. Before the literature contained any clear disclosure of more than these two distinctive crystalline forms of soap, a third type was established by two independent groups of investigators. Research in the Procter and Gamble laboratories had shown that this third form called the 'omega' phase, accounted for a large proportion of commercial soap. Peculiarly enough, the first published description of the 'omega' phase happened to appear in a patent to Mills covering a process, which had been found to produce an unusually small proportion of this phase. The Mills' patent was issued in September, 1942. Shortly thereafter McBain and de Bretteville, as a result of experiments with single pure soaps in anhydrous condition, an-

[34] R. H. Ferguson, *Oil and Soap, 21,* 6 (1944).

nounced the existence of a so-called 'gamma' form and some months later
announced a more complete description of the same soap. The question of
the possible identity of the 'gamma' and 'omega' forms is not considered
in the papers of McBain and de Bretteville, but careful consideration of the
x-ray diffraction patterns, and of the method of preparation of the samples
examined, leaves little room for doubt that the two are essentially the same."

Ferguson then proceeds to call this form the "omega" phase and discards
the term "gamma" altogether. He then announces the discovery of a fourth
form, the "delta," which has been described by Ferguson, Rosevear, and
Stillmann. These four forms are well characterized by the distinctively dif-
ferent crystal lattice spacing, as established by the x-ray diffraction method.

As to the properties of these crystalline phases of hydrated curd soaps, Fer-
guson states that the crystalline phases present in a soap product depend on
the fat, moisture, and electrolyte composition of the system. But this is not all:
the processing methods used to make the product may exert considerable in-

TABLE III-1

X-RAY DIFFRACTION DATA OF THE FOUR SOAP PHASES[34]

Phase	Lattice spacing, A., d/n
Alpha	2.45 and 3.65
Beta	2.75
Delta	2.85 and 3.55
Omega	2.95

fluence, not only on the phases finally present, but also on the condition or
state of these phases. Such factors as the crystal size, orientation, and co-
herence between crystals may vary widely, and bar soap properties, for
example, may be influenced by these factors. Thus, it is usually difficult to
give strict comparisons of soap property for the various phases because, in
general, the same conditions will not have prevailed during their produc-
tion, and, consequently, factors other than phase affect the properties of the
products.

For example, when neat soap is cooled, a mixture of phases may result.
As a general rule, very rapid chilling induces the formation of "omega"
crystal phase, while slow cooling increases the amount of "beta." The melting
properties and the final melting point of the product will depend on, and vary
with, the phases so produced. The firmness of the bar or cake will be affected
by the coherence of the crystals, crystal size, etc., so that the effect of phase
on firmness and other properties may be obscured by many other factors.

The working or agitation of plastic soap compositions induces profound
changes in properties. Soap milling and extrusion are examples of such
processing methods. Extrusion of soap through an orifice, or intense mixing,

enables a closer approach to phase equilibrium. As an example of the changes produced by extrusion, the results in Table III-2 should be noted.

On the other hand, soap of the same fat composition as described in Table III-2, but containing only 6% water and 70% "beta" with only 30% "omega" phase can be reconverted into soap containing 75% "omega" when worked by a sufficient number of extrusions. At the same time, the lathering quality is reduced from 2.1 units to 0.5 unit.

As to the influence of moisture on the stability of the different modifications, Ferguson states that, for instance, sodium palmitate was found to be able to exist in the "beta" phase over the very wide range between hydrates with 2.4% water up to 95%, while the "omega" had a much more restricted range. (This may account for the very high grade lathering quality of

TABLE III-2.

CHANGES OCCURRING BY REPEATED EXTRUSIONS
(19% H_2O, 80% Tallow, 20% Coconut Soap)[34]

No. of extrusions through small orifice at normal temp.	Phase present in soap	Lather (rel. amt.) of soap rubbed off bar at 70° F.	Firmness (arbitrary units)
0	omega	0.20	6.7
10	75% beta		
	25% omega	0.87	8.2
30	95% beta		
	5% omega	0.91	8.3

"stearic acid" made from animal fats and known to contain large quantities of palmitic acid.) The opposite condition exists with coconut oil soap. In this case the "omega" phase dominates.

As to the different lathering qualities of the various soap products according to their history, we would like to recall the suggestion of Thiessen (Sect. 1) according to which the character of cleavage planes many influence the behavior of soap crystals.

(5) Behavior of Crystalline Phases in Soap as Shown by Rheological Evidence

Ferguson shows that crystal phase transition definitely influences the hardness of the soap. In 1945, Vold and Lyon[32] investigated different commercial soap samples under varying conditions by a rheological method, using an instrument called "the cutting wire plastometer." The *practical yield value* is defined as the force in grams per centimeter at which flow becomes observable. The wire is first pushed gently 2–3 mm. into the sample to eliminate the effects of any surface skin. Counterbalancing weights are then removed until the wire begins to move with a velocity not greater than 1 mm. in 5

minutes. This weight, expressed in grams per centimeter of cutting wire of 0.0206 cm. radius, is taken as the yield value, provided that the motion can be stopped and started again by adding and withdrawing 10-g. weight.

Measurement of the yield value of samples originating from the same kind of soap, but having varying thermal history, revealed that considerable influence might be exerted on the hardness of soap by the type of heat treatment.

Three samples were prepared. One was a bar of a framed soap (containing 33.5% water, 1.89% salt, equivalent weight of fatty acids 263.1, iodine value 43.1, cooled from soapboiler's neat soap over a period of 3 to 4 days). The other two bars were prepared by keeping the soap between 90 and 105°C. for 1 hour in the pressure tank, followed in one case by cooling to room temperature over a period of 3 to 4 hours, and in the other by quenching the tank for 30 minutes in ice water. Samples were kept 24 hours in closed containers at room temperature before determining yield values.

The results show that the original bar was the softest, the slowly cooled bars were of intermediate hardness, and the quenched bars were the hardest. According to Vold and Lyon the results are best interpreted in terms of differences in orientation and crystal size in the different samples. It is well-known that the mechanical properties of fibrous materials (cellulose, nylon, etc.) are greatly influenced by the degree of orientation of the micellar units. With many materials the strength increases with increasing degree of orientation. If a cake of soap consists primarily of an interlocked mesh of fibers, as in dilute systems, then a similar dependence on orientation might be expected.

However, the molecules in soaps are perpendicular to the fiber axis (see Fig. III-7), whereas, *e.g.*, in cellulose, the main valency chains are parallel to the fiber axis. Consequently, when a perfectly oriented soap sample is cut at right angles to the fiber axis, the break is primarily between relatively weakly linked hydrocarbon chains, without breaking primary valence chains. This leads to the prediction that in the case of soaps the yield value would become less, the greater the degree of orientation of the sample.

The rheological data are in accord with this hypothesis. The degree of orientation obtained in a solid soap is greater, the slower the rate of cooling from a molten or liquid crystalline state. Correspondingly, we find the slowest cooled soap to be the softest and the quenched sample the hardest.

The patent literature maintains that undisturbed cooling of soapboiler's neat soap usually results predominantly in the formation of "gamma" phase (called "omega" throughout the patent; see also Section 4), but that agitation below T_c during cooling results instead in the "beta" phase. (The definition of T_c is given in Chapter IV, Section 5A and will be dealt with in detail later.)

"Beta" soap produced in this way is said to be much softer than "omega" soap ("Gamma"). Subsequent work recognizes more explicitly that degree of

orientation, size, and coherence of crystals may have as great an effect on the firmness as the nature of the phase present (Ferguson, as quoted in Section 4). Differences of this type due to the different processing must be the explanation for the fact that "beta" soap studied in the later investigations was found to be harder than the "gamma" ("omega") soap.

Table III-3 summarizes the contradicting statements made by Mills, Ferguson, and Vold and Lyon.

Vold and Lyon summarize their opinion by admitting the contradictory evidence by different workers at the present juncture, but stating: "It thus appears that, at least with framed soaps in this range of composition, orienta-

TABLE III-3

DATA ON CRYSTALLINE PHASES OF SOLID HYDRATED SOAPS

Observer	Thermal or mechanical condition	Phase	Hardness	Orientation
Mills	Slow cooling, no agitation	Omega (gamma)	Hard	
	Slow cooling, agitated below T_c	Beta	Soft	
Ferguson	Rapid cooling	Omega	Soft	
	Slow cooling	Beta	Hard	
	Rapid cooling from dilute solution or extrusion at high moisture content and high molecular weight	Delta		
	Mechanical working of omega	Beta	Hard	
Vold-Lyon	Slow cooling	—	Soft	Well oriented
	Rapid cooling	—	Hard	Poorly oriented

tion factors arising from differing thermal history have a more important effect on the observed hardness than the question as to which of the several possible phases is present in greatest abundance."

In the same paper, the authors take sides in the discussion of whether the classical conception of bar soap consisting of "fibers of the more insoluble soaps enmeshing a gel or sol of the more soluble soap" (Sect. 4) should be replaced by the conception of Ferguson as being "made up solely of crystalline phase without any apparent separation of liquid crystalline or liquid phase; the crystalline phase being in the form of a solid solution of the various constituent soaps, and existing in one or more several possible crystalline modification." Rheological investigation favors the second conception, but the authors add that McBain has also long distinguished between what he called "wet curd" and "dry curd," only the former having any free soap solution enmeshed in the solid cake.
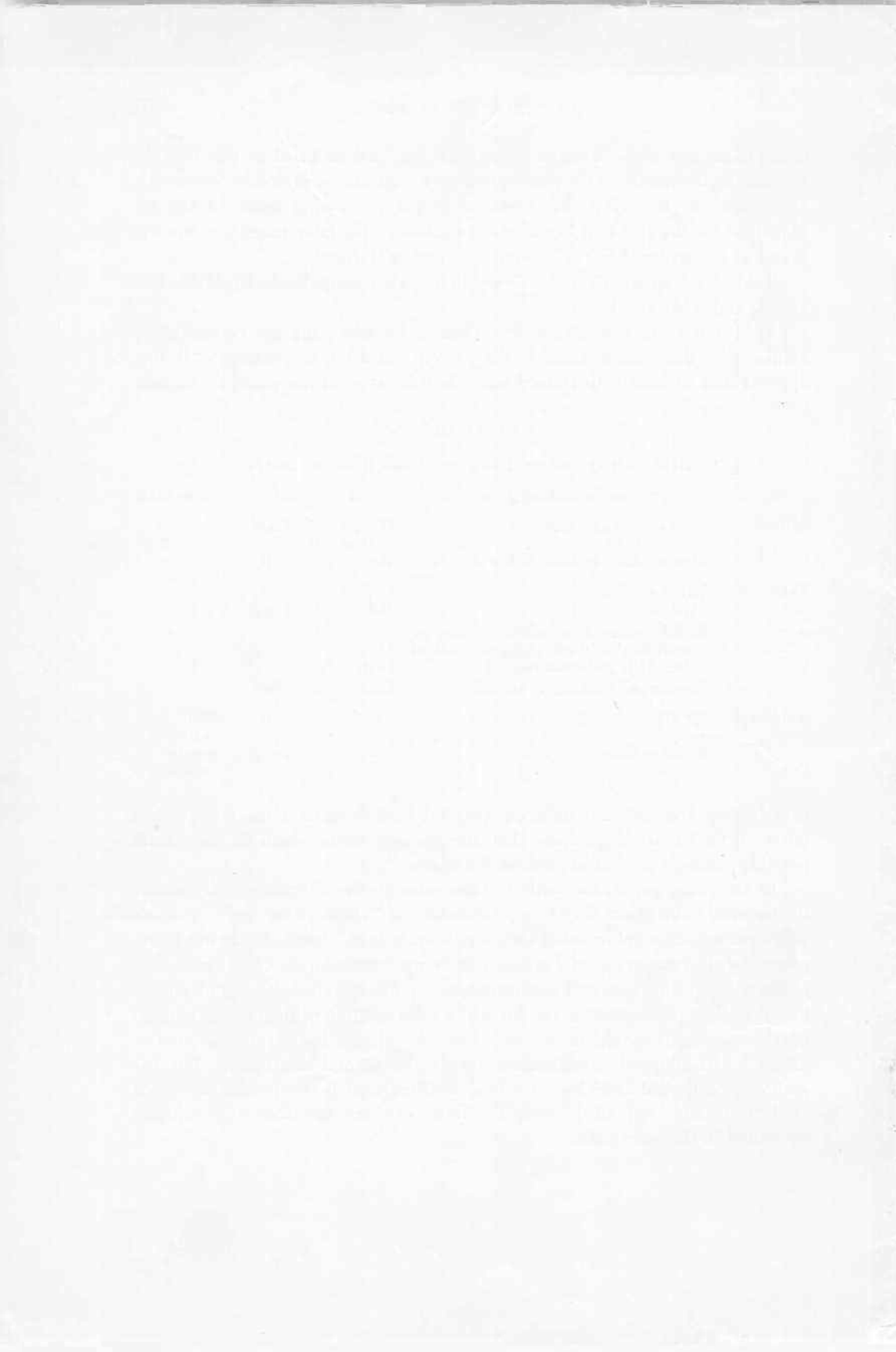
PHASE BEHAVIOR OF SOAPS

(1) The Mesomorphic Phases of Anhydrous Soap

Up to now we have dealt with the completely solid state of soap, with anhydrous crystals and hydrated curds, and the crystalline phases mentioned have all been *solid crystals*, that is, crystals having true and well-defined melting temperatures.

However, there are many conditions in soap technology especially at higher temperature, and at lower temperature in solution, when the crystals formed belong to the class of "liquid crystals."

Solid compounds exist which change only gradually into the liquid state. Between the incipient melting and the final melting points there are in such cases a number of transitional phases, each characterized by distinct phase boundaries and their respective transition points. The body in such phases is not considered totally solid and the condition is termed the *liquid crystalline* or *mesomorphic* state (intermediate form). Soap is a typical body that produces such mesomorphic phases and the temperature at which this state actually occurs ranges from the genotypic point, which is for commercial soaps somewhere between 40 and 50°C, up to the complete melting point around 250°C.

A study of mesomorphic substances established that there are two main classes of such bodies, one called *smectic* (soaplike) and the other type *nematic* (threadlike).

In the smectic state, normal liquid flow does not occur: the movement is of a gliding nature, in one plane. On clean glass surfaces there is a tendency to form "stepped drops" and the edge of the liquid often shows a series of fine lines, visible in ordinary light, but more distinctly so in polarized light. If

the drops of liquid are touched, the gliding movement is observed.   The result
suggests a structure consisting of a series of planes, one on top of the other.
This is supported by the fact that although smectic liquids give an x-ray defrac-
tion pattern, they do so in one direction only.   In the smectic state we
may compare the molecular arrangement to a number of hair brushes in
which the bristles are naturally parallel in each brush, but the brushes are
set at random in space, placed one on top of another.

The molecular groups in the nematic state have been compared to a
bundle of cigars in which the individual cigars can move up and down while
remaining parallel.   See Fig. IV-1.
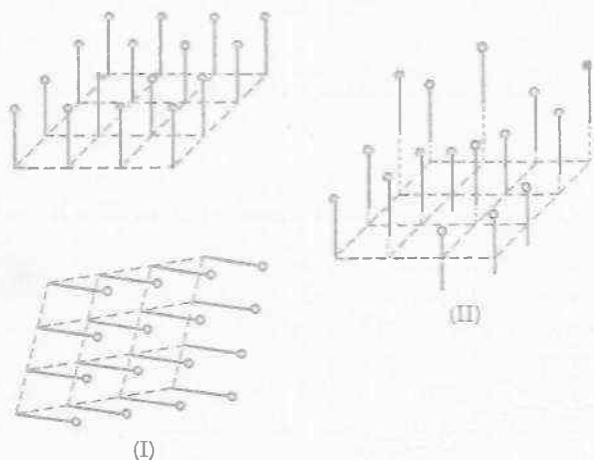
Fig. IV-1. Molecular arrangement in the smectic (I) and in
the nematic (II) mesomorphic states.[35]

Whether or not crystals are present in a system can be investigated by op-
tical means.   An amorphous body (glass or water) gives free passage to
light and is called isotropic.   Of all crystal systems only the cubic system is
isotropic.   Crystals belonging to other systems are *anisotropic,* as a ray of
light entering into it would emerge split into two components; it is therefore
said that such crystals show double refraction.

If a convergent beam of white polarized light is passed through a section
of a uniaxial crystal, cut perpendicularly to the optical axis, and examined
through a Nicol prism, a characteristic interference pattern will be observed.
Thus, an isotropic liquid would produce no pattern in crossed Nicol prisms,
but a uniformly blackened picture, while an anisotropic liquid, that is, a liquid
in which liquid crystals are present, would be detected by a characteristic
pattern.

With the help of such optical methods and, as it will be seen later, also by

other methods, a series of mesomorphic or liquid crystalline states of soap were discovered. One of the most helpful nonoptical methods is the technique of dilatometry.

Whenever we heat a pure isotropic liquid (a completely molten material), measure the volume of dilation occurring in, say, cubic millimeters per 100 grams of liquid, and plot these values *vs.* the values for each temperature difference, we will obtain a straight line when connecting the individual points. But when some kind of transition from one phase into another takes place during the experiment, this transition will become evident by breaks in the straight line, which would be called the *dilation curve* in this case.

The dilatometric measurements of Vold and his associates[36-38] on anhydrous sodium palmitate are reproduced in Fig. IV-2. Subsequent breaks

Dilatometer reading (arbitrary units)
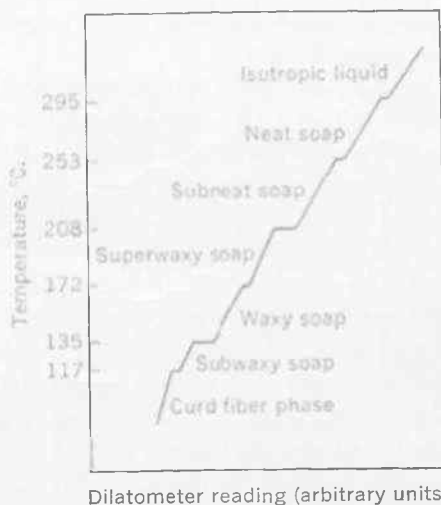
Fig. IV-2. Mesomorphic phases of anhydrous sodium palmitate as distinguished by dilatometric data.[35]

can be observed along the dilation curve in the range below 117°C. and up to the true melting point of 295°C. Each period between two breaks belongs to one of the mesomorphic phases: curd fiber phase to 117°C., subwaxy to 135°C., waxy to 172°C., superwaxy to 208°C., subneat to 253°C., and neat soap phase to the melting point of 295°C., above which the sodium palmitate transforms into the completely molten isotropic liquid. The soap in these various phases has been analyzed optically as well, and the photomicrographs

[35] R. D. Vold, *Soap, 16*, June 1940, p. 32.
[36] R. D. and M. J. Vold, *J. Am. Chem. Soc., 51* 808 (1939).
[37] M. J. Vold, M. Macomber, and R. D. Vold, *ibid., 63*, 169 (1941).
[38] R. D. Vold, *ibid., 63*, 2915 (1941).

show characteristic features as seen under crossed Nicols.

Vold also describes visible differences between some of these phases when observed by simple visual methods. Curd fiber phase is a hard, opaque, white solid, which, if previously melted, forms a cake impenetrable to a stirring rod. There is very little visible change at the transition to subwaxy soap, although, if the soap has been largely freed of air bubbles by previous melting, it is possible to notice a slight decrease in opacity and a certain swelling of the soap against the glass. Although very stiff, it is just possible to push a glass rod through a lump of subwaxy soap. There is no marked change in appearance between the three waxy phases, subwaxy, waxy, and superwaxy soap, although there is the usual tendency for the soap to become softer as the temperature is raised. The next group of two phases, subneat and neat, is very much less viscous than the group of waxy phases, the neat soap, especially, flowing under its own weight. Both are translucent rather than opaque, the sub-neat soap being rather chalkier than neat soap.

It should be emphasized at this point that the term "neat soap" is used here for the last phase before melting to the isotropic liquid and may have nothing in common with the hydrous soap which is formed in the soapmaker's kettle when fitted from a homogeneous soap solution. According to the original suggestion of Vold, this latter phase is called "soapboiler's neat soap" throughout this part of the book.

The "hot wire method" allows one to observe under the microscope the phases spread out side by side on only one sample of soap. With this method, soap spread out into a layer of 2 mm. is kept under an electrically heated wire, allowing for a temperature gradient of a range between 140 and 350°C. The phases develop below the wire according to the temperature range and they can be observed under the microscope between crossed Nicols or by the use of a device known as a mikropolychromar (see *Journal of the American Chemical Society*, 1941, volume 63, page 162).

The anhydrous sodium salts of lauric (C_{12}), myristic (C_{14}), stearic (C_{18}), arachidic (C_{20}), behenic (C_{22}), and oleic (C_{18}, unsaturated acid), potassium stearate, and several other soaps were also studied by the same methods. All underwent a large number of transitions before melting to isotropic liquids, thereby showing that in general the single soaps can exist in any of seven (or eight—more phases are still being discovered) different equilibrium forms depending on the temperature. In general, the transition temperature decreases with increasing chain length, except for the transition from subneat to neat soap, which occurs at a slightly higher temperature the longer the hydrocarbon chain. For example, sodium palmitate melts from waxy to superwaxy soap at 172°C., while sodium behenate undergoes the same transition at 158°C.

In a later review, Vold[15-38] adds that, as the number of carbon atoms in the molecule increases, the temperature of final melting to isotropic liquid

decreases, while that of the formation of a mesomorphic phase from the crystal increases; that is, the temperature range in which the mesomorphic form exists is gradually narrowed down. Presumably, a soap with sufficiently high molecular weight would exhibit but one melting point.

Mixtures of individual soaps behave like single soaps. In the isotropic solution, neat and subneat phases, all pairs of soap studied were completely miscible, even when the two components differed in chain length by six carbon atoms. In the subneat phase, sodium oleate and stearate seemed not completely soluble in one another.

It has been observed at the same time that small additions of one soap to the other usually causes the lowering of the transition temperature. The temperature at which curd fiber phase of sodium palmitate melts to subwaxy soap is lowered from 117 to 107°C. by the presence of 12% sodium laurate. This occurrence may cause the shifting of the transition temperatures of commercially important mixtures down to a range between 100°C. and room temperature.

But even if such lowering of the transition temperatures does not proceed into ranges which are important with our present soap-boiling practices, it is obvious that, with the tendency in our day to switch over to one of the new continuous soapmaking processes, all of these, without exception, working at temperatures far above 100°C. and, as a rule, in the vicinity of the true melting point of soap, the knowledge gained of these mesomorphic modifications emphasizes their importance.

As to the structure in which these mesomorphic modifications appear, Vold states that neat soap (the liquid crystalline form stable at temperatures just below the final melting point) probably has a smectic structure, but whether the remaining mesoforms of soap have the same structure cannot be stated with authority at this time. However, Lascary and Seck are of the opinion that all of the mesoforms are examples of the smectic state, but this must be taken with some reserve.

A recent x-ray investigation found evidence that in sodium oleate solution an orientation of parallel molecular aggregation exists in which the thickness of one layer is equal to the length of one double molecule plus a sheet of water placed between the hydrophilic —COONa groups. McBain[39] presents this in the following words: "Direct x-ray evidence has been obtained for the presence of lamellar micelles in aqueous soap solutions, the soap molecules being closely packed side by side and placed in pairs end to end, just as in soap curd." Stauff[40] finds that the sideways packing may correspond to liquid crystal rather than to crystal structure.

The mention of liquid crystals as present in soap solutions suggests a prob-

[39] J. W. McBain, in *Advances in Colloid Science*, Vol. I, Interscience, New York, 1942, p. 124.

[40] J. Stauff, P. A. Thiessen, *et al.*, *Naturwissenschaften*, 27, 213 (1939); *Kolloid-Z.*, 89, 224 (1939). Through J. W. McBain, ref. 39, p. 124.

ably very wide range of existence of smectic arrangements in all kinds of soap agglomerations.

(2) The Mesomorphic Modifications of Hydrated Soaps and Soaps in Solution

In the investigation of the ranges in which the various mesomorphic phases of anhydrous soap may occur, the thermal method of measuring the dilation in addition to some optical methods was used. It has been shown (Fig. IV-2) that each of these successive phases exists only within a certain temperature limit and by a decrease in temperature one phase simply changes into the lower one in sequence. While existing in one phase, the homogeneity is never disturbed and no separation whatsoever into different layers occurs. The mesomorphic phase in which the anhydrous soap appears depends consequently only on the temperature of the system and, at any given temperature, the phase to which the soap belongs is therefore definitely determined. It will be readily understood that pure anhydrous soap is a system with only one component containing nothing else than soap, and in these circumstances temperature is the only variable.

The position becomes quite different when soap becomes hydrated even to the smallest extent. In this case the system contains two components, water and soap. In addition to temperature changes, the system also becomes variable by changing the proportions between the soap and water present. A whole series of mesomorphic modifications is possible, but it is considerably more complicated to establish the interrelationship between the variables of the system and the conditions in which each of the phases attains stability.

It will probably be useful at this point to present precise definitions for the concepts mentioned here: *phase, component,* and *degree of freedom.*

A *phase* is any homogeneous and physically distinct part of a system which is separated from other parts of the system by definite bounding surfaces.

The number of *components* of a system in equilibrium is the smallest number of independently variable constituents by means of which the composition of each phase present can be expressed, either directly or in the form of a chemical equation.

The number of *degrees of freedom* of a system is the number of variable factors, such as temperature, pressure, and concentration (or composition) which need to be fixed in order that the condition of a system at equilibrium may be completely defined.

It may be added that *equilibrium* is a state or condition of rest in which a system will persist when the variables are fixed.

The *phase rule* is a mathematical expression representing the interrelation existing between degrees of freedom, number of components, and number of

phases, and, is represented by the following equation:

$$F = C - P + 2$$

where F is degree of freedom, C is the number of components, and P is the number of phases.

In the following studies we shall discuss the meaning of the phase rule and show how the data resulting from the phase rule may be recorded on phase rule diagrams and the way in which these phase rule diagrams are able to serve the student of soapmaking in acquiring a deeper knowledge of the processes.

The phase rule expresses in chemical language the algebraic principle that n equations are needed for an unequivocal determination of n independent variables. It further states, in our case, that the phase condition in which soap will appear must be independent of its previous history and will be dependent only on temperatures, the composition of the phase, and pressure. The same state should be reversibly attainable from higher and lower concentrations or from higher and lower temperatures.

There has been considerable discussion (especially in the German literature) as to whether the phase rule is applicable to colloids like soaps. By a very large amount of experimental work carried out in the most systematic manner by J. W. McBain and his school during the last 30 years, it can be considered as established beyond doubt that all experimentally traceable phase procedures satisfy the requirements of the phase rule, and that all soap systems existing in equilibrium with their various phases can be recorded satisfactorily in the usual two- or three-component phase diagrams.

(3) Phase Diagram

There is the ordinary rectangular two-coordinate system in which two variables can be recorded and in which to any point of the area two values are coordinated, one on the horizontal axis (abscissa) and one on the vertical axis (ordinate). The mesomorphic transitions of anhydrous soap are recorded in a phase diagram in Fig. IV-2 where the change of dilation (abscissa) with temperature (ordinate) is demonstrated. The horizontal straight section in this diagram indicates that a state of transition is going on from one mesophase into another.

Another example is Fig. IV-6, vapor pressure (ordinate) *vs.* soap concentration (abscissa), in which, as will be seen later, the horizontal straight sections indicate the simultaneous presence of two phases and a process of transition from one into the other. In this case, of course, the variation of temperature cannot be recorded since a third coordinate is not available for this in a two-coordinate system, and so each curve is able to represent only the conditions characteristic for one fixed temperature. Such curves are called isotherms.

There is a type of binary (or two-component) phase diagram representing the two-component soap–water system in a temperature–soap-in-water concentration system (Figs. IV-4 and IV-5). In these systems, for instance, the T_i values (the temperature at which isotropic solution separates liquid crystals or precipitates curd fibers) and T_c values (temperature at which clear anisotropic liquid and liquid crystalline phase soapboiler's neat soap and middle soap–precipitates white curd fibers) can be recorded. The T_i and T_c curves constitute phase boundaries in themselves; in such coordinate systems the phase areas of the different homogeneous (in which only one system exists without any separation) and heterogeneous (in which any composition must separate into two layers each belonging to one of the adjacent pure phases) phases can be represented.
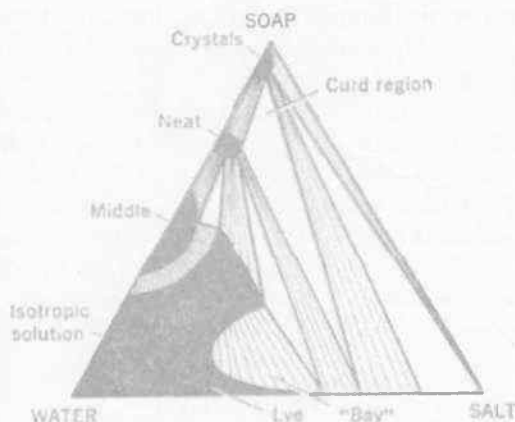
Fig. IV-3. A schematic equilibrium diagram for a system soap–salt–water near 100°.[41] The corners represent soap, water, and salt, respectively, and the compositions are proportional to the distance from these corners.

On studying the influence of salt on the system, the areas must sometimes be shown in which at a fixed soap–water concentration and salt content, a homogeneous phase may exist. These are isotherms as shown, for example, for the phase boundaries of isotropic solutions in Fig. IV-15.

Triangular equilibrium isotherms are used, as a rule, for three-component systems such as the practical soapboiling equilibria between soap, water, and salt (Fig. IV-3).

Each point in such a diagram gives, by its three-coordinate system, the composition of the system with regard to the three components, the sum of which always totals 100. The black areas represent the homogeneous phase, the hatched areas represent a two-phase separation, and the white triangles in

[41] J. W. McBain, R. D. Vold, and M. J. Vold, J. Am. Chem. Soc., 60, 1666 (1938).
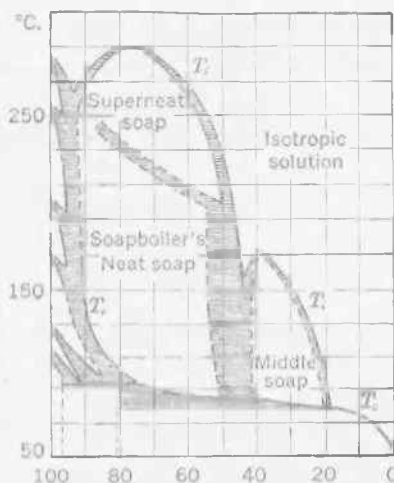
Fig. IV-4. Binary phase diagram for sodium stearate.[45]
Abscissa, weight per cent of soap.

between represent where separation in three layers may be expected, or
where three phases may coexist.

The ternary system may be presented in a somewhat different form, in
which each point gives the coordinated values for water-free soap and salt by
vertical projection so that 100 less the sum of both indicates the water content.
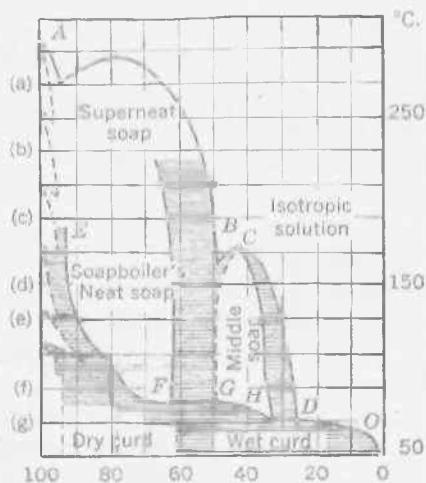
Fig. IV-5. Binary phase diagram for sodium palmitate.[45] Ab-
scissa, weight per cent of soap. (a) Neat. (b) Subneat. (c)
Superwaxy. (d) Waxy. (e) Subwaxy. (f) Supercurd. (g)
Curd.

(4) Soap Phases in Hydrated Systems

Before explaining the methods by which phase boundaries have been established, we will present the exact definitions of the different phases and their nomenclature in soap systems as they are used today in the literature and in actual practice.

From an optical point of view, soap systems must be classified into three large groups: (*a*) clear optically neutral liquids (isotropic); (*b*) clear, or translucent, but double refracting liquids (anisotropic); and (*c*) soft or solid white masses.

In order to avoid possible misunderstanding in the denomination of the individual phases, the equivalent German terminology, as given by McBain, Vold, and Vold,[41] is summarized.

In two (soap–water) and three (soap–water–salt) component systems the following phases are known to exist:

(*a*) Clear isotropic solution called *niger* and *lye*. The niger contains relatively less salt and more soap, the lye generally less soap and more salt. There is a region in the three-component phase diagram which is called the *bay region,* where an equilibrium between niger and lye may exist and where generally the homogeneity of the isotropic solution is disturbed and it is then separated into two layers. The viscous niger, in such cases (upper layer with more soap), would be called *Leimniederschlag,* the liquid lower layer *Unter-lauge.* It must be borne in mind that the region of the isotropic solution embraces a very large area from low to very high temperatures. Soap can be transformed into an isotropic liquid by dissolving it in sufficiently large quantities of water or by heating it in the anhydrous state to high temperatures where, above its true melting point, it would become an isotropic liquid, even when no water at all is present. Isotropic liquid is defined by the complete absence of solid or liquid crystals, and the special optical feature as mentioned above is the absence of any turbidity when observed directly, or a total blackout when observed in polarized light (under crossed Nicols).

(*b*) (*1*) *Neat soap* (soap boiler's neat soap). This phase is a visually clear translucent liquid. When tested optically, it is found to be double-refracting anisotropic, and therefore is a "liquid crystalline phase." Soapboiler's neat soap fitted and settled is hot and liquid neat soap (the German equivalent is *geschliffene Kernseife, abgesetzte Kernseife,* or *Kernseife auf Leimnieder-schlag. Curd soap (Kernseife auf Unterlauge),* which is a completely salted-out soap, is understood (for the time being by the authors) to be, while hot and liquid, the same phase, namely neat soap, except where the concentration of electrolyte is high enough to cause separation of curd fibers (true solid crystals); these appear in any case upon cooling.

(*2*) *Kettle wax.* This phase was not known when the classification was given by McBain (1938). It is now probable that the phase present when

salting-out to curd constitutes "kettle wax," and the conceptions as described under (1) for curd soap should be interpreted accordingly.

(3) *Middle soap.* This is another conic (smectic) anisotropic liquid or clear double-refracting liquid crystalline phase, immiscible with neat soap and of lower soap content. It has been, sometimes mistakenly confused with niger (*Leimniederschlag*) which is, however, wholly different, and is present in the kettle when bunching occurs.

(c) *Crystalline phases.* These are soft or solid white masses.

(1) *Lamellar crystals* seldom occur in sodium soaps, but more often in potassium and ammonium soaps. In soft soaps they form the fig (*gekoernte Schmierseife*). They also appear in the sediment of acid soaps and probably in acid soap preparations like shaving creams. Since they generally are not found as a stable phase in the case of sodium soaps, they do not appear in phase diagrams shown in this book.

(2) *Curd fibers.* This is the common crystalline form of sodium soaps. Often referred to as "hydrated crystals." They are the white fibers, or *Kern-fasern*, often several centimeters long, but usually consisting of bundles of fibers which are ultramicroscopic except in length. Curd fibers may be anhydrous, but they generally contain water.

The foregoing represents a classification of separate and well-defined phases that may occur in hydrated soap systems in equilibria. McBain, in his classification[41] defines *soap curd* or simply *Curd* as follows. "Soap curd should not be confused with commercial curd soap boiled on lye (*Kernseife auf Unterlauge*) and also not with "curd fiber." Soap curd is a solid mixture of phases containing curd fibers, with or without solution or liquid crystalline material. "Dry curd" consists entirely of curd fibers.

(5) Methods for Establishing Phase Boundaries

(A) T_i AND T_c CURVES

When considering the three big groups into which hydrated soap systems may be classed when their properties are determined by optical methods, a combined thermal and optical method for this purpose appears expedient. A soap solution must be completely isotropic, that is, totally devoid of any truly or liquid crystalline elements when heated to a sufficiently high temperature. In that state, it must be completely transparent and must produce a blacked-out picture when investigated under crossed Nicols. When gradually cooled, there must be a temperature obtained at which some turbidity may appear due to the formation of a second phase, and the liquid will show under crossed Nicols a pattern which reveals the presence of liquid crystals. This will be the temperature transition point at which this particular soap–water composition changes from the pure isotropic phase into the mixed anisotropic region, and this transition point will be termed T_i. When further

cooled, there will be a second transition point, T_c, at which the first visible white curd precipitation appears. By establishing T_i and T_c for a series of different soap–water compositions, two curves, the T_i and T_c curves, may be recorded in a two-component phase rule diagram.

The T_i and T_c points have been established in practice by (a) visual observation of the temperature and concentration at which new phases appear and disappear and (b) observation with the microscope and the polarizing microscope with heat stage by (1) analysis of the separated phases, (2) the vapor pressure method, and (3) by dilatometric data.

These T_i and T_c curves constitute part of the phase boundaries. The T_i curve represents the temperatures for each soap concentration at which clear isotropic solution enters into the heterogeneous area in which isotropic solution may exist in heterogeneous equilibrium with neat or middle soap. The T_c curve, in turn, represents the boundary under which pure neat or middle soap or pure isotropic solution may form heterogeneous equilibria with curd soap.[42]

The experimental determination of the T_i and T_c value appears to be quite simple and consists in sealing off the different soap–water mixture samples with their varying composition in a glass tube, converting the samples to homogeneous isotropic solutions by heating them to a sufficiently high temperature, and later making a double determination on each sample for establishing T_i and T_c, respectively. T_i will be given by the temperature at which the clear isotropic liquid separates another birefracting phase when cooled slowly, and T_c by the temperature at which the last traces of white curd have disappeared on slow heating of the solid samples.

The curve through points $ABCDO$ in Fig. IV-5 represents the T_i curve, and $EFGHDO$ the T_c curve. It will be noted that at the composition ranges from F–G and from H–D the temperature of disappearance of crystalline soap becomes constant, that is FG and HD are straight lines.

At this stage, application of the phase rule can be instructively demonstrated, and, at the same time, a classical example given as to how McBain and his associates[43, 44] furnished the proof that the phase rule is applicable to practical soap equilibria.

By direct application of the phase rule, it can be deduced that four phases must be present in each of these two regions. When the phase rule

$$F = C + 2 - P$$

is substituted by the data as follows:

$$C = 2 \text{ (soap and water) and } P = 3$$

[42] J. W. McBain, G. C. Brock, R. D. Vold, and M. J. Vold, *J. Am. Chem. Soc.*, **60**, 1870 (1938).

[43] J. W. McBain, *et al., J. Am. Chem. Soc.*, **60**, 1870 (1938).

[44] *Idem.*, **63**, 875 (1941).

then F would be equal to 1, meaning that one degree of freedom remains, or one factor remains variable. This means, in turn, that to each soap composition a still variable temperature could be coordinated as it is on the branch between E and F.

But when P is assumed to be 4, no freedom will be left in such a system, and therefore, in this case, the temperature must be constant while four phases exist. This would be the meaning of the straight line between FG and HD.

What are these four phases on the straight branches? Between F and G, neat, middle, crystalline curd, and vapor phase. Between H and D, middle, isotropic, curd, and vapor. It can be seen from the phase diagram that on the curd branches only three phases may exist as neighbors: neat soap, curd, and vapor phase between E and F; middle soap, curd, and vapor between G and H; and isotropic solution, curd, and vapor between D and O.

The presence of vapor as a separate phase in watery solutions must always be taken into consideration. In this way, a seemingly one-phase system of one liquid component must be considered to be in reality a two-phase system containing one liquid phase and the vapor above it constituting the other phase.

The methods by which the phase diagram has been completed and the T_c curve verified were also based entirely on the requirements of the phase rule.

(B) THE VAPOR PRESSURE METHOD

In the case of two components only (soap and water), and in case of one liquid phase (actually two phases: one liquid plus one vapor), there will be two degrees of freedom left, since $C = 2$, $P = 2$, and $2 - 2 + 2 = 2$.

Any two variables such as soap concentration and vapor pressure may be chosen as the two degrees of freedom. This means that in a coordinate system where the vapor pressure appears on, say, the vertical coordinate and the soap concentration on the horizontal coordinate, both values will be able to vary freely along a curve for any one fixed temperature. However, when two independent liquid phases are present, the number of freedoms must drop by one, and, in this case, as long as the two liquid phases exist simultaneously, the vapor pressure must remain constant while soap concentration is varied. As soon as either of these liquid phases disappears, the vapor pressure will again be able to vary, and the straight part of the diagram will start to curve again.

This is one of the methods by which McBain and his school[45] investigated large areas of temperature–soap–water concentration equilibria in which the different phases may exist in homogeneous or as coexistent heterogeneous phases. The vapor pressure of various pure soaps with different soap content in the solution or, which is the same, the relative humidity in the air above such soap systems, has been determined for several fixed temperatures, and

[45] J. W. McBain and W. W. Lee, *Oil and Soap*, **20**, 17 (1943).
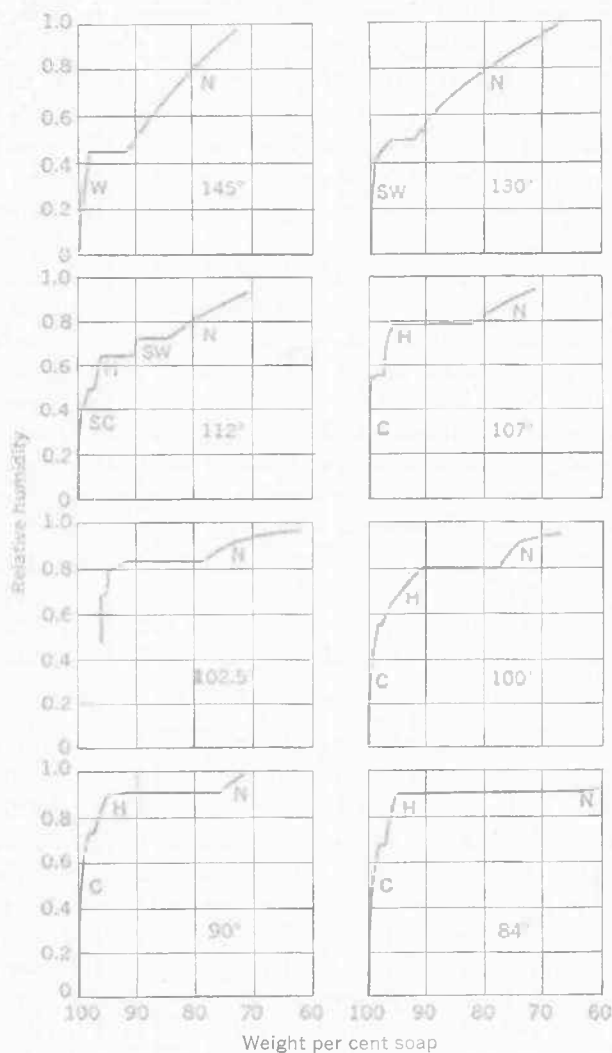
Fig. IV-6. Relative humidity (P/P_s) *versus* soap concentration isotherms for hydrated sodium palmitate.[45]

the isotherms are recorded in a coordinate system of relative humidity versus soap concentration. (Fig. IV-6.)

Let us consider the isotherms for pure sodium palmitate in Fig. IV-6. The isotherm for 84°C. starts in the lower left corner as for all the curves with anhydrous soap (it will be remembered that the first fixed temperature recorded in the dilatometer curve in Fig. IV-2 was 117°C., and there it was stated that anhydrous sodium palmitate appears in the "curd fiber phase").

It has been observed by McBain and Lee that anhydrous sodium palmitate appears in the "curd phase" at 83°C. On hydrating the anhydrous soap the relative humidity rises continuously up to the concentration of 96.8% soap or 3.2% water content, which corresponds to a composition of one molecule of sodium palmitate with one-half molecule of water. Such a compound may be called *half-hydrate* or *hemihydrate,* and it can be seen that when this composition is reached at 67% relative humidity the curve suddenly becomes straight (one degree of freedom drops out), showing that there is a phase boundary and that for a little while two phases are present simultaneously. Then, on further hydration, the curve starts to rise again, representing the exclusive range of the hemihydrate modification. At 92% soap concentration there is a very long straight section which finally reveals a phase boundary at 64% soap, this time the lower boundary of the "soapboiler's neat soap." Let us follow now the 90°C. isotherm where three phases are present successively from 100% soap down to 70%: curd is transformed into hemihydrate in about the same region as before, and then the hemihydrate transforms into soapboiler's neat soap when hydration reaches 76% soap. In this case also there are straight sections between the areas of homogeneous regions showing the existence of heterogeneous phases between the two adjacent homogeneous areas.

TABLE IV-1

RANGE OF COMPOSITION FOR THE STABLE EXISTENCE OF HYDRATED SODIUM PALMITATE
AT A SERIES OF TEMPERATURES[45]

Temp., °C.	Phase	Weight per cent soap
84	Curd	94–100
	Neat	(64)–75
90	Supercurd	94–100
	Neat	62–76
100	Supercurd	90–100
	Neat	(65)–77
102.5	Neat	(62)–78
107	Supercurd	95–100
	Neat	(70)–81
112	Supercurd	94–100
	Subwaxy	90–92
	Neat	(61)–84
130	Subwaxy	96–100
	Neat	(68)–92
145	Waxy	97.5–100
	Neat	(70)–92

In addition to the methods described here, several others were also used, x-ray, dilatometric, calorimetric, and optical. By applying the potentialities of all of these methods, McBain *et al.*[45] succeeded in securing in the course of

thirty years sufficient information to explore almost the entire area of the binary phase diagram.

Table IV-1 contains the information derived from the vapor pressure diagram concerning the range of composition for the stable existence of phases on hydrated sodium palmitate at a series of temperatures.

McBain and his co-workers finally compiled all of this information in temperature–concentration diagrams, which may be called the "complete binary phase diagrams of various pure soaps" (Figs. IV-7, IV-8, IV-9).

The usefulness of such phase rule diagrams is obvious. In the first place,
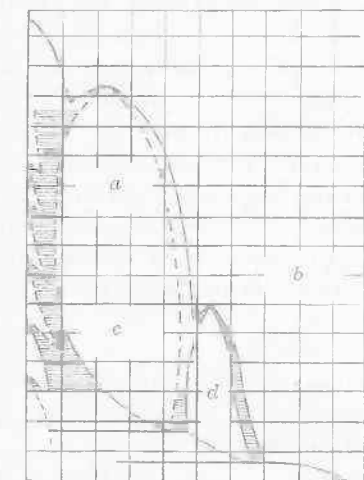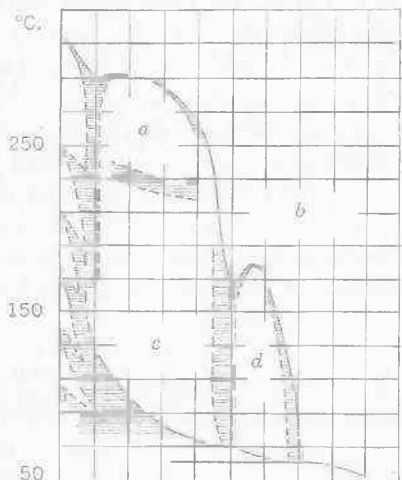
Fig. IV-7   Fig. IV-8

Fig. IV-7. Binary phase diagram for sodium laurate.[45] Fig. IV-8. Binary phase diagram for sodium myristate.[45] (a) Superneat soap. (b) Isotropic solution. (c) Soapboiler's neat soap. (d) Middle soap.

they contain all the information concerning the water-free soap as given in Fig. IV-2. In the second place, all the transition points and phase ranges for anhydrous soap may be read from the ordinate.

(C) How to Derive Information from the Binary Phase Diagram

Few general indications should be given for the use of the binary diagrams in the areas representing the hydrated soap. The white enclosed areas represent temperature and soap concentration ranges in which only one homogeneous phase exists like soap boiler's neat soap, superneat soap existing at very high temperatures, middle soap, isotropic liquid, and dry curd. There are the small areas of low hydrated modifications like supercurd, subwaxy, waxy, superwaxy, subneat, and neat, which also consist of homogeneous areas.

The shaded bands show the horizontal isothermal tie-lines along which hetero-geneous two-phase systems exist. Thus, wet curd may be taken, for instance, as an area in which dry curd co-exists with isotropic liquid or middle soap.

Let us consider some practical examples from the diagram for pure sodium palmitate (Fig. IV-5).

We will be able to predict the result when, at a certain temperature, an-hydrous soap is hydrated to different degrees. Let us first take the practically important temperature of 100°C. We see that at this temperature the region of soapboiler's neat soap will be reached at 76 grams of dry sodium palmitate with 24 grams of water up to the ratio of about 65 grams of soap and 35
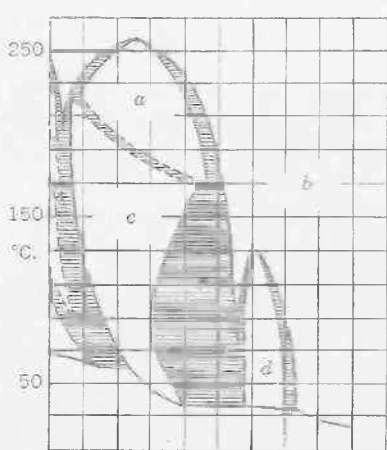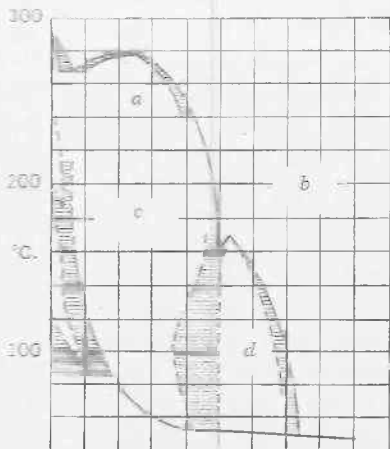
Fig. IV-9   Fig. IV-10

Fig. IV-9. Binary phase diagram for sodium oleate.[45] Fig. IV-10. Binary phase diagram for a commercial soap.[45] (a) Superneat soap. (b) Isotropic solution. (c) Soapboiler's neat soap. (d) Middle soap.

grams of water. It can also be seen that, when adding water at 100°C., a separation in two layers will take place after a while; the upper layer will be pure neat soap and the lower layer will be middle soap. Then, at a ratio of about 50 g. of soap and 50 g. of water, we will obtain a homogeneous layer consisting of the dense and viscous middle soap so much feared by the prac-tical soapmaker. Again, mixtures between 45 parts of soap and 55 water and 28 parts of soap and 28 parts of water will separate into two layers, the upper one being pure middle soap and the lower one pure isotropic soap solution containing less than 28% of soap.

Let us now take a pure neat soap containing 65% of sodium palmitate at 100°C. We would like to know what happens when this soap is cooled

slowly.   On following the 65% vertical line we will learn that the mass will remain clear neat soap down to a temperature of 82°C.   It will then transform into heterogeneous curd and then, at 70°C., into dry curd, which is a completely crystalline phase.   The point at 82°C. will represent the T_c point in this case.

Such binary phase diagrams for soap–water systems have been worked out for sodium laurate, myristate, stearate, and oleate, and in view of the very large amount of information incorporated therein, we have reproduced them here for further reference.

In addition to the 5 pure soaps, McBain and Lee investigated a commercial toilet soap base (Fig. IV-10).   A phase diagram had also been worked out for this product.   Here, however, the possibility must be taken into consideration that such a commercial soap may separate into fractions under certain conditions, thereby increasing the number of components, and upset the assumptions made for the application of the phase rule.   It was established, however, that the phase rule can be applied with satisfactory results, to practical soap-boiling equilibria as well.

This phase diagram characterizes the individual soap throughout all ranges of temperatures and concentrations.   There may also be certain specific points derived from the diagram which are very suitable for serving as reference points for comparing soaps from different fat compositions.   McBain proposes such a characteristic point, for instance, as the point of lowest temperature at which 70% neat soap (containing 62% fatty acid as soapboiler's neat soap produced in the kettle) can exist alone, which is identical with the T_c point to 70% neat (compare Fig. IV-5); the lowest temperature and the corresponding soap concentration at which neat soap can exist at all (point F); the left boundary of temperature for neat soap on the 100°C. horizontal line; and the "temperature of ready solubility" (the temperature at which soap suddenly becomes highly soluble—to an extent of 20–30% soap-in-water; a few degrees lower the solubility was only slight).   This point is situated on the boundary line between isotropic solution and the mixed zone of middle soap and isotropic solution, but above the isotropic–curd boundary; consequently, this point represents at the same time the lowest temperature at which middle soap is still able to exist (T_s).

(D) Effect of Small Quantities of Salt on the Phase Boundaries

Up to this point the effect of electrolytes on the equilibria has not been taken into account and the diagrams given deal only with systems of pure soaps or soap–water solutions.   It is evident from what has been said about the role of components in the phase rule that when a new component enters the system the phase diagram will have to undergo a change.

McBain, Vold, and Gardiner[46] established the phase diagram for various

[46] J. W. McBain, R. D. Vold, and K. Gardiner, *Oil and Soap*, *20*, 221 (1943).

TABLE IV-2

COMPARISON OF SOME IMPORTANT VALUES FOR FIVE PURE SOAPS
AND THE TYPICAL COMMERCIAL SOAP[45]

Soap	T_s	T_c for 70% neat	Lowest T for neat		Soap left in T_c boundary for neat at 100° C., %
			T, °C.	% soap	
Na laurate	42	76	62	58	80
Na myristate	60	84	70	51	79
Na palmitate	71	88	80	53	78
Na stearate	77	91	83	50	79
Na oleate	32	43	34	61	86
Toilet	49	60	51	58	85

soap–water concentrations of sodium oleate to which the constant addition of
1.5 parts by weight of sodium chloride to 100 parts of sodium oleate were
made. They have chosen this proportion because at this proportion neat with
70% soap would contain 1.05% salt, and this is about the upper limit of salt
content which still occurs with soaps in practical soapboiling.

This time the technique for establishing the main phase boundaries was
based entirely upon the determination of the T_c and T_i points. The results of
these determinations were laid down in a double phase diagram.

By comparing the two phase diagrams, the effect of the addition of small
quantities of salt to soap may be summed up as follows.

(a) It lowers the solubility of the solid soap in all phases (starting at the

TABLE IV-3

TEMPERATURE OF READY SOLUBILITY (T_s) OF VARIOUS SOAPS IN WATER, AND SOLUBILITY
OF SOAPS IN WATER IN PER CENT BY WEIGHT AT 90° C., INCLUDING SODIUM
SOAPS OF VARIOUS SINGLE OILS AND FATS[46]

Soap	T_s	% soap at 90° C.	Max. % salt in niger
Na laurate	42°	36	11.2
K laurate	17	36	23.6
Na myristate	60	30	—
Na palmitate	71	26	5.4
Na stearate	77	19	2.8
K oleate	> 0.9	26	9.5
Na oleate	32	30	3.2
Palm oil	52	31	4.6
Whale oil, semihardened	—	35	5.2
Green sulfur olive oil	27	33	3.5
Tallow	53	29	4.2
Soybean oil	—	34	2.9
Coconut oil	—	42	13.3
Tallow–coconut oil	.48	28	—
¾ palm, ¼ coconut oil	49	—	—

horizontal at 88° C., the curve of the system without salt will be reached at about 79% soap, the curve representing the mixture with salt only at 73.7% soap; likewise, by following a vertical line of one fixed soap concentration, say at about 70% soap, on lowering the temperature the curd phase will be reached earlier when salt is present than when it is not).

(b) It enables the neat soap to take up more water without changing into the isotropic solution. This can be seen from the shape of the upper T_i curve, which is bulged out when compared to the pure binary curve. This effect would be even more important between neat and middle soap regions, as this would mean that in the presence of salt the danger of forming middle soap phase is diminished. The fact that such an effect exists is well-known by the practical soap boiler and was shown by Ferguson. However, no such conclusions can be drawn from the present curves.

(c) The area of middle soap is narrowed, and against this the solubility of soap in isotropic solution is increased.

(6) The Complete Ternary Phase Rule Diagram

(A) METHODS FOR ESTABLISHING BOUNDARIES IN THE TERNARY SYSTEM

The two-component rectangular diagram contains only the information necessary to follow the phase behavior of soap systems containing soap and water. The three-component diagram has been established by the following methods.[47]

(1) Weighed samples of pure soaps (sodium laurate, stearate, etc.) were mixed with weighed quantities of salt and the amounts made up to 100 by water, and sealed into a Pyrex tube. These samples were prepared in such variety as to cover the largest possible area in the phase rule diagram. On these samples the values of T_i and T_c were observed as already described.

(2) At the same time, the samples were observed at temperatures T_i and T_c to determine which of the phases is being formed under these conditions on cooling or heating over the temperature limits of T_i or T_c. This was established by visual methods.

(3) In order to have the details worked out in certain cases, so-called delimiting experiments have been carried out at one fixed temperature. This method consists in preparing, by trial and error, pairs of systems whose compositions lie very close together, one on each side of the boundary to be determined, and placing the boundary between them.

(4) Some of the systems which under the observed conditions separated into layers belonging to different phases were centrifuged at the temperature of equilibrium in order to obtain the most complete separation of the phases and then chilled by quenching in a Dry Ice mixture. Samples of phases

[47] J. W. McBain, *et al.*, *J. Am. Chem. Soc.*, *60*, 1874 (1938).

separated in this way (which previously were in heterogeneous equilibrium) were analyzed for their soap and salt contents.

(5) The respective volumes of the phases separated were estimated, thus acquiring knowledge of the quantitative aspects of phase separation.

As a result of these micro and macro experiments ternary phase rule diagrams were obtained. Fig. IV-11 shows the ternary diagrams for sodium
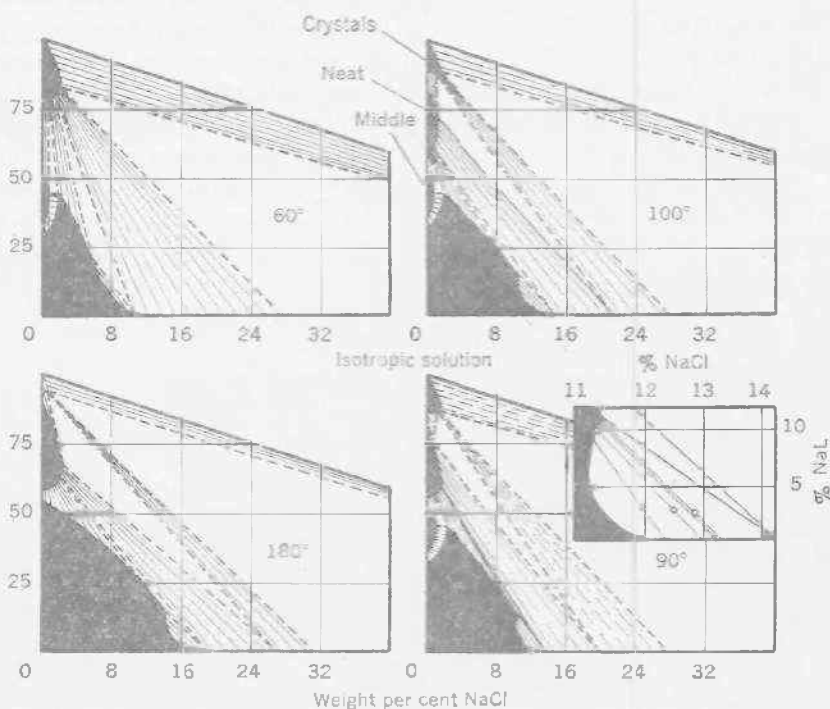
Fig. IV-11. Ternary phase diagram for sodium laurate at four different temperatures.[47] Ordinate, weight per cent of sodium laurate.

laurate at four different temperatures, each temperature requiring, of course, its separate triangular diagram.

The diagrams are of the type explained in Sect. 3; each point is characterized by a fixed amount of anhydrous salt and soap, the difference from 100 being water. The black areas represent homogeneous phases. The hatched ones containing tie-lines are the heterogeneous areas in which a two-layer separation is to be expected; the white triangles are areas in which three phases have been found to be in equilibrium. The equilibrium always exists between two phases connected by one tie-line, or in the case of a three-phase equilibrium between the pure phases connected by the three corners of a white triangle.

McBain succeeded at this stage in again confirming the applicability of the phase rule diagram to soaps. At the same time, a very important practical use could be demonstrated for this type of diagram. The following experiments were carried out with certain soap and salt compositions which would be situated in the so-called "bay" region of the ternary phase diagram. (Fig. IV-11; 90° isotherm in upper right corner.)

The "bay" region represents a two-phase niger–lye system corresponding to the soap mass that can be found in the soapboiler's kettle beneath soapboiler's neat soap and which, on standing, separates into two layers, niger and lye. In a phase rule diagram, a certain soap–salt system situated on a tie-line connecting two homogeneous phases should separate into two layers whose weight ratio will be inversely proportional to the distances measured along the tie-line from the point representing the initial composition to the phase boundaries. This could be checked easily by the experiment described above in which, in addition to the composition of the layers, their volume has also been established.

TABLE IV-4

DATA OF THE EXPERIMENTS IN THE "BAY" REGION[47]

Initial system (% by wt.)		Niger (A) Na laur.	Lye (B) NaCl	Lye (B) NaCl	Weight A/weight B	
Na laur.	NaCl				Calc.	Obs.
10.0	11.3	10.9	11.13	13.36	12.5	12
3.0	12.8	10.9	11.13	13.36	0.34	0.25
4.9	12.3	10.8	11.12	13.23	0.81	0.68
3.0	12.45	10.3	11.10	12.96	0.39	0.34
3.0	12.0	9.0	11.06	12.38	0.43	0.45
				(Na laur. 0.2)		

Table IV-4 contains the results of these very important experiments and show that: (a) the relative weight of the separate layers corresponds with the length measurements made on the tie-lines in the diagram, and (b) the separated niger and lye layers both had compositions representing the border compositions of the related phases.

The good corroboration between assumption and experimental result allows us to believe that by using phase rule data we shall be able to predict the following for any soap system of a known initial composition at a particular temperature: (1) whether it will separate at all into phases; (2) into how many phases it will separate; (3) what the relative quantities of each separated phase will be; and (4) what the composition of each of the phases will be.

It should be mentioned that such calculations can be carried out theoretically for three-phase areas as well (e.g., for neat–niger–lye), and that these

calculations are then based on the compositions representing the three corners of the triangle.

However, it must be clear that, in order to be able to predict all these particulars with sufficient accuracy for all practically possible soap equilibria, it would be necessary to study all of them with exactness with which McBain and his associates proceeded in the case of sodium laurate. A tremendous amount of investigations lies ahead, with all of the fat compositions, electrolyte concentrations, and temperatures that are used by the soap boiler.
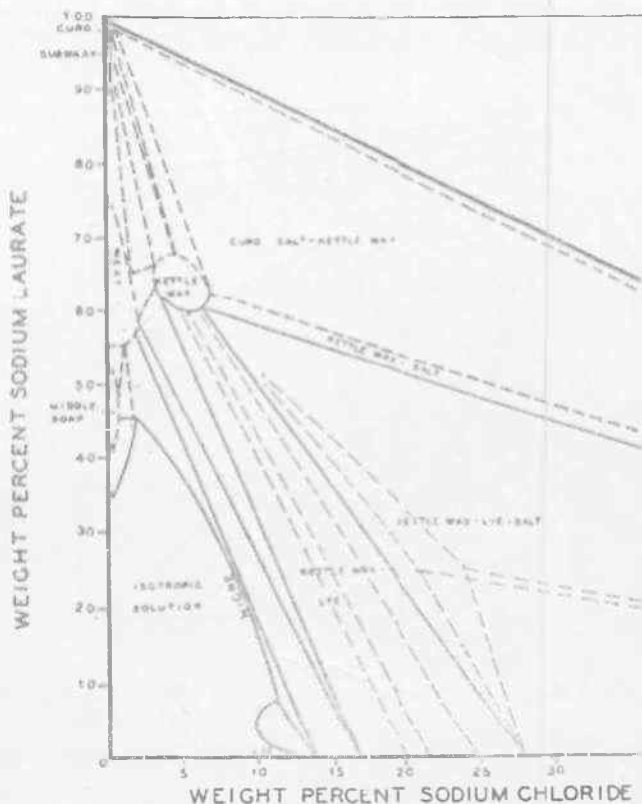
Fig. IV-12. Phase diagram of the system sodium laurate–salt–
water at 90°, showing kettle wax island.[49]

(B) THE KETTLE WAX PHASE

During 1944, a new liquid crystalline phase, the kettle wax island, was discovered.[48] Its boundaries were confirmed by the sinthetic delimiting method explained just above. The exact position of this new homogeneous

phase island can be seen from the new triangular phase diagram in Figs. IV-12[49] and IV-13.[48]

The waxlike kettle wax phase appears as an island in a dominant position; the tie-lines show its equilibria with lyes containing between 4.2 and about 21% NaCl. The phases present are curd, supercurd, crystalline salt, kettle wax, neat soap, middle soap, and isotropic soap solution, which includes lyes. Triangles represent equilibria between three condensed phases and are separated by heterogeneous regions of two condensed phases. Broken lines are provisional or inaccurately determined positions.

An interesting feature of this new phase is that, upon cooling, the island drops gradually into deeper concentration regions, moves toward higher salt
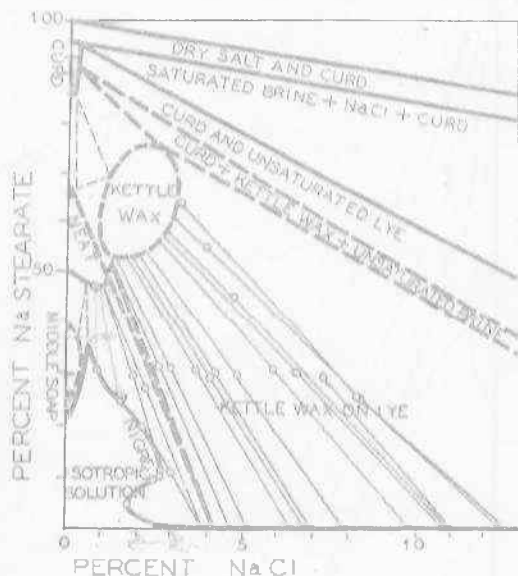
Fig. IV-13. Phase diagram of the soap system sodium stearate–salt water at 90°C.[48]

concentrations, and becomes smaller in area. At 80°C. it becomes a very small spot in the diagram.

The most important feature of this discovery must be seen in the fact that the new island is now interposed in the middle of the diagram between the curd phase and the lye phase. With sodium laurate there are now no tie-lines at all between the curd and the lye phases, and, with sodium stearate, curd is only connected with very highly concentrated salt lyes.

[48] J. W. McBain, K. Gardiner, and R. D. Vold, *Ind. Eng. Chem.*, 36, 808 (1944).
[49] J. W. McBain, R. C. Thorburn, and C. G. McGee, *Oil and Soap*, 21, 227 (1944).

(C) The Phase Diagram and Explanation of Some Aspects of the Practical Soap-Boiling Process

The new ternary diagrams for sodium laurate and stearate give a general idea of what is happening during the individual stages of the practical soap-boiling process; boiling, fitting, setling, and graining. Until the discovery of the kettle wax phase, the phenomena of soap-boiling processes were explained as occurring in equilibria between isotropic liquids (niger and lye), anisotropic, or liquid crystalline solutions (neat soap and middle soap) and crystalline substance (curd) only.

The new diagrams show that there are connecting tie-lines between the homogeneous neat and niger region, especially in the low salt concentration area. Saponification, fitting, and settling can be explained, therefore, by equilibria existing between these phases. The facts that no tie-lines at all exist between curd and lye with sodium laurate, and sodium stearate is only connected with lyes of high concentration, gives evidence that the conception of salting-out the curd on lye was based on a false assumption and that, in fact, whenever sodium laurate or a mixture containing sodium laurate is salted-out the system kettle wax – on lye is produced. The position is similar with sodium stearate where the kettle wax island is likewise almost engulfed by the heterogeneous phase of kettle wax – on lye. But in this case there are, in the other part of the diagram at least, some tie-lines connecting curd with highly concentrated salt solutions, thus allowing the formation of systems of curd on concentrated lye.

The discovery of the kettle wax island again furnishes a very interesting indirect demonstration of the validity of the phase rule and the phase diagram for all soap systems. It was always assumed that the homogeneous phase formed when salting-out to curd is the same phase as soapboiler's neat soap. The results of analytical determinations on samples from the soap layer in the grained-out condition of palm oil, soybean, and tallow soaps were all found to be too high in salt content to fit within the soapboiler's neat soap boundary and too low in soap content to be identical with curd as shown by the old phase diagrams. When looking at the diagram of sodium laurate as it was given in 1939 (Fig. IV-11), the area which is now occupied by the kettle wax island was meant to be the area of two- and three-phase heterogeneous systems. Therefore, it was not comprehensible at that time that the relatively low soap- and high salt-containing systems produced by graining out, and which could be neither neat soap nor curd, should nevertheless be a homogeneous system.

Since kettle wax was unknown at that time, this high salt content was assumed to be caused by the fact that the glycerine of the charge was still present in the system when the samples were taken. It can be concluded today, however, that the contradictions were due to the existence of kettle wax.

During graining-out, the salt and water content is higher than in any other step, and they are actually in the range of kettle wax existence. The operations following in the sequence of the soap-boiling process (boiling, fitting, and settling) are all within the region of neat soap – niger equilibrium, and the results from analyses on samples taken from these stages fit into the phase diagram.

(7) Solubility of Various Soaps in Salt Solutions as Seen from the Phase Diagrams

(A) THE AREA OF ISOTROPIC SOLUTION

We will now consider only that part of the phase diagram which shows the boundary between homogeneous isotropic solution from one side, and curd, middle soap, soapboiler's neat soap, superneat soap, etc. from the other side.

It is obvious that the size of the area of the homogeneous isotropic solution can be taken as a measure for the solubility of a certain individual soap in salt solutions. Every point outside this area will represent either soap belonging to another homogeneous phase or a mixture of separated phases about to separate into layers. Figs. IV-14 and IV-15 show such sections from phase diagrams of sodium stearate and of some other individual soaps.

The first thing we can determine from these diagrams is that the area of homogeneous isotropic solution increases with rising temperature. Sodium oleate is more soluble in salt solution than sodium stearate.

The size of the enclosed area in Fig. IV-15 clearly demonstrates the big difference in the solubility of the various soaps in pure water and also in salt solutions of varying strength. The values at the vertical axis give the solubility of the various soaps in salt-free water. It is interesting to note that the highest solubility is not in all cases obtained in salt-free water.

(B) COMPOSITION OF THE NIGER

The isotropic soap solution existing at $90°$C. in the soap kettle is identical with what is called "niger" industrially. The boundary of the enclosed black area will consequently represent the composition of the niger at varying concentrations for the soaps being considered.

The diagram for sodium stearate (Fig. IV-14) demonstrates, for example, that a low salt addition (1.5%) extends the area of the homogeneous isotropic liquid. Following the boundary curve, we observe that the more salt is added, the smaller becomes the quantity of dissolved soap in the niger. At the maximum of 2.8% salt in the niger, we reach the "Bay" region, in which the niger is separated into two liquid layers, one containing much more soap than the other, but not differing greatly in salt content. The lower part of the isotropic solution extends into a region in which almost no soap is present and in which the separated layers consequently must be the "lye."

(8) The Phase Rule in Mixed Soap Systems

Commercial soap contains, as a rule, a mixture of sodium salts of high and low molecular weight fatty acids. The phase rule diagrams of sodium laurate differ considerably from diagrams of soap of other fatty acids. These differences are especially very marked when comparing the region of the niger boundaries for different individual soaps.

It was important, from a practical point of view, to establish in which manner the presence of sodium laurate would influence the phase behavior of a high molecular saturated soap. Such mixtures prevail in nearly all tech-
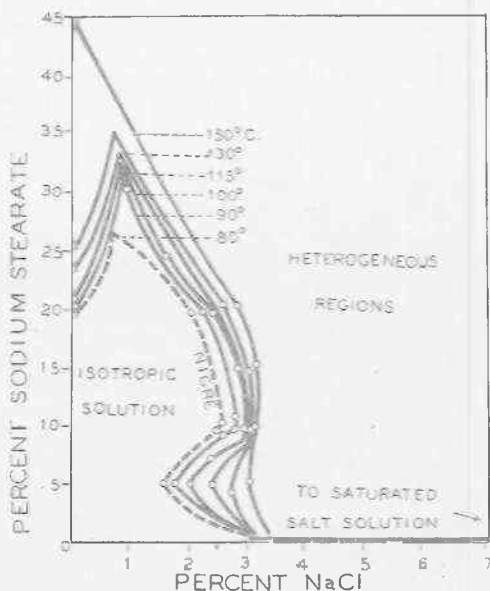
Fig. IV-14. Boundaries enclosing homogeneous isotropic soap solutions which contain sodium stearate–water–salt, at 80 and 150°C., respectively.[48]

nical soaps. In order to investigate this problem, the boundaries of the isotropic liquid with mixtures of sodium palmitate and sodium laurate have been studied.[50]

The conclusion which may be drawn from these experiments is that corresponding phase boundaries occur nearer to the value of pure sodium laurate than to pure sodium palmitate. This effect is due to interference of the shorter sodium laurate molecule with the degree of regularity of the sodium palmitate micelles. In the words of the author, mixed micelles of smaller size, less

[50] J. W. McBain, R. D. Vold, and W. T. Jameson, *J. Am. Chem. Soc.*, *61*, 30 (1939).

orientation, and greater solubility must be produced by the occurrence of the shorter laurate molecules among the longer homologs, which is an example of mutual solubilization.

Means have been worked out to calculate the additional salt concentration necessary to add to that required by the phase diagram of pure sodium palmitate in order to obtain the corresponding phase boundary when a mixture of sodium palmitate and sodium laurate is present.
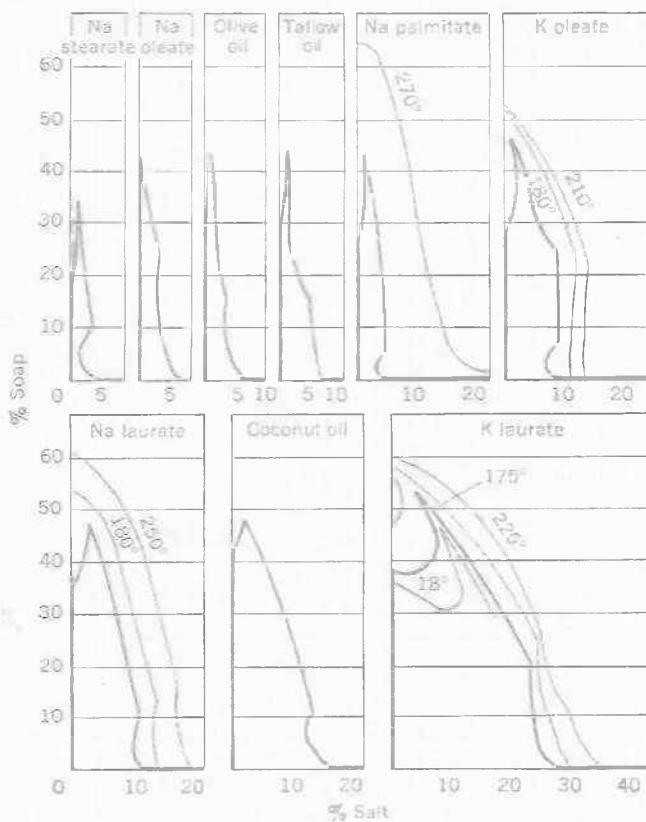
Fig. IV-15. The boundary of isotropic solutions of various soaps containing added sodium or potassium chloride at 90°C.[46]

(9) Influence of Alkaline Electrolytes on the Phase Behavior of Soap

Recently, a technically important phase study was published[50a] in which the boundaries of the isotropic solutions for a number of mixtures of a commercial soap with various alkaline builders were investigated.

[50a] R. C, Merrill, *Ind. Eng. Chem., 39*, 158 (1947),

The commercial soap had the following characteristics: average molecular weight of fatty acids, 273; iodine value, 48.4; 0.62% NaCl; 0.046% excess Na_2O on dry basis.

The following conclusions are drawn by the author from these experimental data.

The data given show that the salting-out of soaps by these electrolytes, some of which are alkaline as well as colloidal, is a complete process. All electrolytes do not behave in the same way, even on a molecular basis. The salting-out of nonassociated electrolytes of low molecular weight involves a reduction in the amount of water which acts as a solvent, because of hydration of the added ions. The salting-out of soap solutions is complicated by the existence in them of complex equilibria between free ions and various types and sizes of ion aggregates and micelles. The addition of salts is believed to increase the proportion and size of micelles until they link together and precipitate. Because of the presence of neutral molecules in the average micelle, the added salt may be incorporated in it and affect the equilibria involved. The effect of added salts on micelle formation, which can be very specific because of steric and other factors, is probably more important in determining its effect on soap solutions than is hydration of added ions.

The unusually small solubility of soap in Calgon solutions suggests some sort of complex formation. Complexes with soap could also be formed by the colloidal silicates. This may explain the decreased effect, on a molecular basis, of the silicates of higher SiO_2/Na_2O ratio in salting-out soap solutions containing less than 20% soap. Another factor which may be involved is fractionation of the siliceous silicates. The salting-out of soap solutions is also complicated by the multiplicity of crystalline and liquid–crystalline phases which aqueous soap systems form at various concentrations and temperatures.

In spite of the complexity of the subject, sufficient regularities exist so that the data can be used to predict phase diagrams for other soaps and concentrations. The regions of existence of isotropic solutions for other soaps in the presence of all these electrolytes should be predictable to a fairly accurate degree if this part of their diagram is known with any one salt. Phase diagrams at higher soap concentrations for this and other soaps can also be predicted from these data, although with less certainty. One of the practical industrial applications of such work is to predict the amounts of various builders which will dissolve in soaps at crutching temperatures.

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THE PHASE RULE IN PRACTICAL
SOAP-BOILING EQUILIBRIA

(1) Merklen's Practical Conception of the Phase Rule

(A) THE SYSTEM CURD ON LYE AND NEAT SOAP SETTLED ON NIGER

The first to investigate and to try to understand what actually happens in the soap kettle and to consider these processes as equilibria between phases was François Merklen of Marseille.[51] In his classical description of the soap-boiling and forming processes, the theory was expressed, for the first time, that the various layers in the kettle may be regarded as independent phases in equilibrium.

After the oil has been completely saponified, the soap will be thrown out from its solution by salt or, as it is commonly termed, the soap will be *salted-out*. The mass floating as an upper layer on the lye is called *curd* and after it had settled the lye will be withdrawn from beneath. To the curd, which had been retained in the pan, a new, more concentrated salt containing soda lye is added, this lye being called the *strong lye*. Thereupon the entire contents of the pan is boiled, and it will be observed that, after a certain period of boiling, an equilibrium is set up between the soap curd and the strong lye at boiling temperature. The composition of the curd is dependent on the lye concentration, as it may be proved by analyses at the termination of the boiling.

At this point Merklen goes on with his explanation the operator starts to reduce the concentration of the strong lye by gradual dilution with water while keeping the mass continuously boiling. After each addition of water, a new equilibrium will be set up between the two layers: soap and lye. While,

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[51] F. Merklen, *Etude sur la constitution de savon du commerce,* Marseille, 1906; through the German edition by F. Goldschmidt, Halle, 1907.

in the course of this procedure, the lye becomes gradually more diluted, a concentration of the lye will eventually be obtained at which some soap will begin to dissolve in the lye. This lye concentration is a characteristic figure for each kind of soap; this characteristic lye concentration, which is threshold concentration of soap solubility, will be termed in all our future discussions the *lye limit concentration* (L.L.C.).

Continuing the process, more and more water is added and gradually more soap is dissolved by the lye. The original curd, which had been in equilibrium with the undiluted strong lye, has a granular appearance. The granules are distinctly separate from each other. As the concentration of the lye decreases, the small grains of the curd gradually begin to swell, their interfaces become less and less distinguishable, and finally they become united in one homogeneous mass or solution. As this point is reached the lye will have dissolved a considerable proportion of the soap and the condition commonly termed as *fitted* is attained. The pan contents is given a period of rest.

After settling, the upper layer represents *commercial soap*. The layer beneath consists of an alkaline salt solution saturated with soap, and which is called in the language of the soapmaker, the *niger*.

The two liquid phases, soap and niger, are in equilibrium at boiling temperatures. These two liquid phases may be fully united to form a single phase. In order to reach this stage, the pan contents must be boiled and sufficient water added gradually. After the addition of each portion of water, the upper layer will have diminished in volume and the niger gradually increased. At a certain concentration, there will be no upper layer left, and there only one phase will be present. At this stage the separated system will be "closed" again.

The one-phase system may be separated again into two phases by the addition of an electrolyte, *e.g.*, caustic soda or salt.

Merklen regarded the system "soap–niger" as composed of three components (water, soap, and caustic soda) and made up of two phases. He did not take into consideration the vapor phase and, consequently, considered the system as tri-variant (three degrees of freedom); he concluded that for any fixed pressure and temperature the compositions of both phases are dependent only on the quantitative relation of the components present (soap, water, electrolyte). The composition of the two phases in equilibrium will be completely fixed, in his opinion, when in addition to the freedoms—pressure and temperature—a third factor is fixed as well. As a third factor, Merklen chose the concentration of one component—the lye.

Pressure, in soap-boiling routine, is actually fixed by atmospheric condition, and so is the temperature. Consequently, at a fixed lye concentration the composition of the whole system is fully determined. In other words, when carrying out the fitting operation in such a way that the niger contains the same amount of electrolytes at the end of the fitting operation, it is possible to obtain successive batches in which both phases—soap and niger—have identi-

cal compositions, that is, the soap contents in all soap layers and in all niger layers are practically identical.

However, it should be borne in mind that practical soap systems are actually much more complicated, for they are made up of more than three components (soap, water, caustic soda, salt, soda ash, and glycerine), and this probably accounts for the fact that commercial soap always shows considerable variations in composition.

(B) Lye Limit and Fitting Lye Concentrations

From Merklen's point of view, the composition of the fitted and settled soap depends on (1) the nature and colloid structure of the particular soap, which in turn depends on the fat composition, (2) temperature, and (3) composition of the niger.

According to (1), "lye limit concentrations" vary considerably; as a result of (2) the fitted and settled soap in most cases still separates some liquid upon cooling; and (3) the niger separates some alkali and salt containing lye as well. The concentration of this lye separated from the niger is another characteristic, this time for fitted soap, just as the lye limit concentration must be considered as a characteristic figure for grained soaps or lye. This characteristic lye concentration is termed by Merklen the *fitting lye concentration* (F.L.C.).

For the complete understanding of these two terms, we may add that when the lye reaches the L.L.C. the soap will be completely salted out, and the lye will not contain any soap. However, when only a smaller quantity of electrolyte (salt plus soda plus soda ash) is added, the lye will still contain a certain amount of soap and the soap layer will eventually be considered as perfect neat soap. It is this particular equilibrium which Merklen wanted to characterize by the F.L.C. for each soap composition. It should be stressed here that the F.L.C. is not the electrolyte concentration in the niger as such, but rather in that part of the niger which separates from it as lye on cooling.

In Table V-1 data for L.L.C. and F.L.C. are presented which show that there is only a small difference between both for any individual soap.[52]

TABLE V-1

Lye Limit Concentration (L.L.C.) and Fitting-Lye Concentration
(F.L.C.) of Soaps[52]

Soap	L.L.C.		F.L.C.	
	°Be	°C.	°Bé	°C.
Sesame oil	9	20	7.5	23
Poppyseed oil	8.5	23	7	26
Lard	7.75	29	6.75	27
Olive oil foots	14	28	12.25	25
Coconut–groundnut oil	22	16	18.25	14

[52] *Ibid.*, p. 58.

TABLE V-2. Data from Experiments of Merklen[53] (All Figures in per Cent)

Source of soap	Strong lye				Related soap				Limit lye			
	$NaOH$	$NaCl$	Na_2CO_3	Red. conc.*	H_2O	$NaOH$	$NaCl$	Pure soap	$NaOH$	$NaCl$	Na_2CO_3	Red. conc.*
Sesame oil									1.92	3.6	1.89	5.96
Olive oil, rancid	3.02	10.4	1.19	12.63	35.3	0.4	1.72	62.58	1.7	5.8	0.76	7.11
Poppyseed oil (molten)	2.36	15.4	1.4	16.42	27	0.18	1.16	—	2.61	4	1.40	6.76
Poppyseed oil	•7.6	16.6	1.73	22.82	23.6	0.67	1.3	74.43	1.83	4.05	0.86	4.77
Lard	6.68	16.2	3.78	22.57	24.6	0.77	1.42	73	1.53	3.75	1.04	5.28
without NaCl	9.88	1.65	8.42	15.29	30.5	1.64	0.15	67.0	3.92	0.66	3.56	6.27
Tallow	7.84	14.1	3.08	21.49	26.2	0.93	1.26	71.0	2.17	4.0	1.03	6.13
Linseed oil	8.58	12.2	4.32	21.18	25.3	0.85	1.07	72	2.55	3.8	1.4	6.53
Olive oil foots	3.26	15.65	2.38	17.98	31.42	0.73	2.13	65.72	2.67	9.3	1.87	11.64
Saponification olein									2.98	4.4	1.46	7.5
" with glycerine									2.62	5.5	1.19	7.98
Saponification stearine	8.24	7.5	4.48	16.86	—				2.7	2.4	1.4	5.46
Cotton oil	9.84	7	4.97	18.28	26.6	0.73	0.61	72	—	—	—	—
Groundnut oil	10.13	7	5.18	18.67	26.7	0.93	0.68	71	3.26	2	1.78	5.84
Castor and rapeseed oils	13.38	3.2	2.48	17.33								
Coconut and groundnut oil									9.34	1.2	10.64	15.43
Coconut oil									2.57	22.05	0.38	21.95

* Reduced concentration.
  Calculated from the data of Ubbelohde and Rickert.[55]

Merklen was probably the first practical investigator to try to establish the interdependence of the composition in fitted and settled soaps and in the niger. He carried out practical boiling experiments on a 200-lb. scale, which included fitting, settling, and analysis of the soap layer and the lye which separated from the niger on cooling. Unfortunately the quantitative relation between the two phases after separation were not recorded.

(C) MERKLEN'S EXPERIMENTS

Table V-2 contains a summary of Merklen's soap-boiling experiments.[53] Each individual soap and the related lye were analyzed at several consecutive stages and recorded as follows: (1) analysis of the strong lye; (2) analysis of the soap curd in equilibrium with the strong lye; (3) L.L.C. of the individual soap reduced to terms of caustic soda; (4) as discussed in section (d) below; analysis of the lye at the L.L.C.; (5) analysis of the soaps in equilibrium with

[53] F. Merklen, l. c., a summary of the results of his experiments as tabulated by E. L. Lederer in *Kolloidchemie der Seifen*, p. 288.

TABLE V-2 *(continued)*

Source of soap	Related soap				Fitting lye					Related soap		
	H_2O	NaOH	NaCl	Pure soap	NaOH	NaCl	Na_2CO_3	Red. conc.*	H_2O	NaOH	NaCl	Pure soap
Sesame oil	—	—	—	—	1.55	2.8	1.5	4.7	37.05	0.12	0.25	62.58
Olive oil, rancid	—	—	—	—	1.39	5.0	0.65	6.05	44.41	0.16	0.83	54.6
Poppyseed oil (molten)	—	—	—	—	1.35	3.2	0.93	4.5	36.5	0.15	0.21	63.16
Poppyseed oil	—	—	—	—	1.64	3.8	0.86	5.36	—	—	—	—
Lard	—	—	—	—	1.37	3.4	0.9	4.76	4.6	0.15	0.23	65.02
without NaCl	—	—	—	—	2.94	0.5	2.81	4.71	35.5	0.46	0.02	64.02
Tallow	—	—	—	—	1.87	3.4	0.86	5.24	36.1	0.25	0.29	63.6
Linseed oil	—	—	—	—	2.04	2.8	1.15	5.02	35.58	0.2	0.2	64.02
Olive oil foots	—	—	—	—	2.21	7.9	1.51	9.81	33.56	0.32	0.66	65.46
Saponification olein	—	—	—	—	2.12	3.3	1.19	5.55	34.31	0.16	0.18	65.35
" with glycerine	—	—	—	—	1.95	4.2	0.97†	6.06	31.13	0.14	0.18	67.05‡
Saponification stearine	50.48	0.87	0.65	48	—	—	—	—	—	—	—	—
Cotton oil	—	—	—	—	2.94	1.2	1.3	4.6	35.58	0.32	0.06	64.04
Groundnut oil	—	—	—	—	2.45	1.5	1.4	4.41	36.1	0.32	0.06	63.52
Castor and rapeseed oils	—	—	—	—	3.92	2.85	0.97	6.86	34.37	0.41	0.22	65.0
Coconut and groundnut oil	—	—	—	—	7.60	0.9	8.64	12.48	30.68	0.64	—	68.68
Coconut oil	32.06	0.24	1.55	65.75	—	—	—	—	—	—	—	—

† Contains 8.7% glycerine.
‡ Contains 1.5% glycerine.

L.L.C.; (6) F.L.C. of the individual soaps reduced to terms of caustic soda; (7) analysis of the lye at the F.L.C.; and (8) analysis of the fitted soap.

(D) THE "REDUCED" CONCENTRATION

The experiments of Merklen disclosed that the L.L.C. may be produced not only by lyes containing mixtures, but also by individual electrolytes. It could be observed, however, that the various electrolytes exert salting-out actions

TABLE V-3		
RELATED ELECTROLYTE CONCENTRATION (IN PER CENT) GIVEN BY UBBELOHDE AND RICHERT[55]		
NaOH	NaCl	Na_2CO_3
1	1.15	2.11
0.87	1	1.835
0.473	0.544	1

TABLE V-4		
RELATED ELECTROLYTE CONCENTRATION (IN PER CENT) GIVEN BY MCBAIN AND PITTER[54]		
NaOH	NaCl	Na_2CO_3
1	1.21	1.96

quite different in degree. Comparisons between the salting-out efficiency of various electrolytes were made by McBain and Pitter[54] and by Ubbelohde and Rickert.[55] Taking the concentration of NaOH necessary for reaching graining effect as a unit, the concentration of the other electrolytes required for producing the same effect may be expressed in relation to NaOH. In this way, the concentration of each electrolyte may be converted into terms of equivalent NaOH concentration.

Electrolyte mixtures behave like an individual electrolyte whose graining-out efficiency will be somewhere between the efficiency of its components. The "reduced" concentration of the mixture containing 3.02% NaOH, 10.4% NaCl, and 1.19% Na_2CO_3 may be calculated as follows:

$$\frac{3.02}{1} \times \frac{10.4}{1.15} \times \frac{1.19}{2.11} = 12.63 \text{ (in terms of NaOH)}$$

TABLE V-5

Lye Limit Concentrations

Oil	Expressed as			
	NaOH		NaCl	
	Merklen	Bontoux[55a]	Merklen	Bontoux
Linseed	6.53	5.9	7.89	6
Sunflower	—	7.6	—	5
Soybean	—	5.6	—	6
Corn	—	4.6	—	5
Cotton	—	5.3	6.9	5.5
Sesame	—	5.3	6.8	5.5
Rapeseed	—	3.6	4.8	3.5
Peanut	—	4.9	6.7	5.5
Olive oil foots	—	7.3	14.0	6
	—	4.6	—	5
	—	4.9	—	5
Shea butter	—	4.0	—	4.5
Palm	—	4.9	—	5
	—	—	—	11
Lard	—	5.3	6.30	6
Tallow	6.13	4.6	7.0	5
Coconut	—	17.7	25.09	20
Palm kernel	—	—	—	13
Poppyseed	—	—	6.8	—
Castor	—	—	32.8	—
Coconut : peanut (1 : 1)	—	—	21.8	—

[54] J. W. McBain and Pitter, *J. Chem. Soc. London*, 127, 893 (1926).

[55] L. Ubbelohde and Richert, *Thesis*, Karlsruhe, 1911.

[55a] E. L. Lederer, *Kolloidchemie der Seifen*, Steinkopff, Dresden and Leipzig, 1932, p. 278.

(2) The 66% Rule

(A) In Curd on Lye Systems

In the course of analytical investigation of curds and of the corresponding lyes in the normal phase regions of "curd on lye," and of "neat fitted on niger," Wigner[56] found that there is a well-defined relationship between the percentage of salt in the curd, the percentage of salt in the lye, and the contents of the curd in fatty acids. He derived the following mathematical expression for this relationship:

$$\% \text{ FA in curd} = \frac{100 - \frac{100 \times \% \text{ NaCl in curd}}{\% \text{ FA in curd} \times 100}}{1.515}$$

This means that when the salt contents of the lye in equilibrium with the curd and the salt contents of the curd itself are known by analytical determination the fatty acid content of the curd can be calculated. However, the value of the constant $K = 1.515$ had to be established by experiment, and the way in which this has been done can be seen from the analytical material furnished in Table V-6.

TABLE V-6

DATA ON THE 66% RULE IN "CURD ON LYE" SYSTEMS[57]

FA in curd (found anal.), %	NaCl in lye (found anal.), %	NaCl in soap (found anal.), %	K (calc.)[a]	FA in salt-free soap hydrate ($K = 1.515$), %	Free soln. in 100 parts soap[b]	Expt. No.
53.7	9.5	1.76	1.52	66.0	18.7	1
52.3	9.1	1.87	1.52	65.9	20.8	2
54.6	9.0	1.44	1.538	65.0	17.2	3
57.8	8.8	1.10	1.503	66.0	12.4	4
56.0	8.7	1.33	1.52	66.1	15.2	5
53.5	9.1	1.69	1.52	65.7	19.0	6
57.1	8.2	1.17	1.38	66.6	13.5	7
57.8	9.4	1.17	1.42	66.0	12.5	8
58.0	9.1	1.12	1.50	66.2	12.2	9
56.7	9.2	1.34	1.505	66.3	14.0	10
54.7	9.6	1.68	1.51	66.3	17.1	11

$$^a K = 100 - \frac{100 \times \frac{\% \text{ NaCl in curd}}{\% \text{ NaCl in lye}}}{\% \text{ FA in curd}}$$

$$^b \text{Free solution in 100 parts soap} = 100 - \frac{\% \text{ FA in curd} \times 100}{66}$$

On the assumption that his formula is valid for salt-free curd as well,

[56] J. H. Wigner, *Soap Manufacture. The Chemical Processes*, Chem. Publishing Co., New York, 1940.

[57] J. H. Wigner, *l.c.*, p. 40, with some additional data of the authors.

Wigner calculated that such a salt-free curd must contain 66% fatty acids. This is easy to derive from the first formula produced when the percentage of salt in curd is zero. In this case, the whole formula is reduced to:

$$\% \text{ FA in curd} = 100/1.515 = 66$$

The results of this calculation led Wigner to regard soaps which are in equilibrium with their lyes as a mixture of two components. One component is always an electrolyte-free soap hydrate invariably containing 66% fatty acids, and the other component is a certain quantity of "entangled lye" (entrained lye) or "free solution" containing the entire amount of electrolytes present in the soap.

"A soap curd may be regarded as consisting of soap hydrate containing 66 per cent of fatty acids and lye identical in composition to that from which it has separated."

Wigner adds that it is quite immaterial for the purposes to which the rule is applied whether the whole of the lye is mechanically separable or whether a small fraction does form a homogeneous mixture with the true soap hydrate.

In accordance with this concept, curd No. 1 in Table V-6 with 53.7% fatty acids and 1.76% NaCl would be composed of 81.3% of 66% soap hydrate and 18.7% of "free solution" containing 9.5% salt. It can be seen from the table that the curd was grained out from a solution containing 9.5% salt.

The 66% rule also means, when exploring its possibilities in the neat soap – niger systems, that for any value of salt in free solution and of salt in the settled soap there is only one value of per cent fatty acids in the same settled soap.

In Wigner's opinion the rule is found to hold good in any condition that may occur in the course of a normal boil of soap. However, it must be borne in mind that different values have to be given to the various electrolytes, depending on the activity with which they affect the graining-out of soap. (See Section 1.)

In systems "fitted and settled on niger," Wigner offers a definition different from that put forward for curd. He states that such soap is probably "a soap hydrate of a composition which varies according to the concentration of salt in the free solution, always containing more water than the hypothetical 66 per cent hydrate, and containing a small amount of salt which increases with the increase in the degree of hydration."

Nevertheless, the 66% rule is valid for fitted and settled neat soap on niger as well, and this has been shown experimentally by Wigner. Applying the same method in recording Merklen's classical experiments, we shall now quote Wigner in explaining his concept of the fitting-out procedure.

"A knowledge of the nature of the soap curd makes it easy to understand what happens in the operation of fitting. The curd is boiled up with water and, as soon as the percentage of salt in free solution is reduced below a certain limit, it will begin to dissolve soap. If the operation is stopped at this stage, the contents of the pan will settle into two layers, the lower layer now consisting of a weak solution of soap in the free

solution. After each further addition of water, the free solution becomes further diluted, and it becomes capable of dissolving more and more soap. The successive stages are what are known as coarse, medium, and fine fits, respectively, though these phases have no exact significance, but merely denote roughly the appearance of the soap when submitted to the usual test on the trowel. During these stages, the solution, which will form the lower layer, otherwise the niger, dissolves more and more of the soap from the upper layer and thus diminishes the amount of neat soap, which is the main product. At the same time, the composition of the latter also undergoes changes. The neat soap from the coarsest fit, apart from certain exceptional cases, has a high fatty acid percentage, often well over 63%, but this slowly diminishes through the successive stages of increased dilution of the free solution. In ordinary soap pans these changes cannot be continued indefinitely, as the settling into two layers becomes slower and slower, the more the free solution is diluted and, in practice, it is found that a limit is reached when the neat soap contains about 60% of fatty acid [compare with Kawakami's investigation in Section 4]. The fatty acid content of the niger corresponding to this varies somewhat according to the mixture of fats employed, but is usually rather above 40 per cent."

(B) APPLICATION OF THE 66% RULE TO THE STUDY OF PRACTICAL SOAP-BOILING SYSTEMS

In accordance with this description, it must be possible, within limits, to fit a soap to any fatty acid content (or, as it is called, to any required "test") by regulating the salt content in the free solution by the addition of water. The percentage of free salt in solution necessary to obtain a certain type of fit varies, however, considerably according to the nature of the soap charge; the more soluble the soap the higher will be the percentage of salt required. In order to establish exact figures showing the interrelationship between salt in free solution, fatty acid and salt content in the neat soap, and fatty acid content in the niger, small scale or laboratory boils (Vol. II) should be made for each new soap charge and, the results of the determinations should be tabulated and plotted as a suitable graph. The analytical result of such an investigation may be exploited as follows: The determination of fatty acids and salt in the neat soap and in the niger is simple enough after the layers have separated; the salt content in the free solution can be calculated when the total salt contents in the pan are known and the quantity of the free solution has been calculated from the total fatty acid content of the pan. This, in turn, is quite simple, when the whole operation from the beginning has been conducted with a thorough knowledge of the quantities of material involved. We are generally able to know the composition of the curd in the kettle before fitting is started. The quantity of the free solution then is (see Table V-6):

$$100 - \frac{\% \text{ FA in total pan content} \times 100}{66}$$

and:

$$\% \text{ NaCl in free solution} = \frac{100 \times \% \text{ salt in pan content}}{100 - \frac{\% \text{ FA in total pan content} \times 100}{66}}$$

The quantity of salt in free solution can then be recorded from the begin-ing of the operation, when the weight of the curd at the start and the quantities of water added gradually for fitting are known.   The quantity of free solution can be calculated at the beginning together with the salt concentration.   The water added then goes exclusively to increase the free solution and to decrease the concentration of salt in it.

An example of the results obtained on an experimental boil which has been fitted very coarsely and then gradually changed into a finer condition by the addition of measured amounts of water is given in Table V-7.   According to Wigner, this soap was made from an easily soluble fat charge.

TABLE V-7

DATA INVOLVING THE 66% RULE IN THE SOAP SYSTEM FITTED AND SETTLED ON NIGER[58]

Sample	NaCl in free soln., %	Neat FA, %	Soap NaCl, %	FA, % in niger	Type of fit
1	11.0	63.2	0.47	1	Coarse
2	10.9	63.35	0.435	1.2	
3	10.7	63.3	0.425	3.5	
4	10.3	63.2	0.435	9.6	
5	10.25	63.2	0.44	8.6	Medium
6	9.3	62.8	0.445	24.0	
7	8.25	62.35	0.45	32.6	
8	7.85	61.85	0.48	36.2	
9	7.55	61.3	0.53	37.2	
10	7.25	60.85	0.55	39.3	Fine

The figures in Table V-7 can be plotted as "salt in free solution" against "fatty acids in neat soap" and "fatty acids in niger," and by use of the curves obtained we can determine the "salt in free solution" concentration required for any type of fit or, what is the same, for any fatty acid content required in the neat soap.   These curves are given in Fig. V-1.

Actually, this is the most practical method for studying accurately the properties of a fat charge in the laboratory.   There are not many fat charges in use at one time in one factory.   It is a good routine to make one series of experimental boils with each fat charge, and to work out the corresponding curves as shown in Fig. V-1.   Let us consider the curve "fatty acid contents" against "salt in free solution" in Fig. V-1.   Neat soap of any fatty acid con-tent between 60 and 63 can be produced when the salt concentration of the free solution is changed within the limits of 7 to 11%.   It can be seen that the fatty acid content of the niger would decrease, at the same time, from about 40% to almost zero.   This is one of the most valuable pieces of informa-tion the soapmaker can obtain, and it gives him the means of adjusting his

[58] J. H. Wigner, *l.c.*, p. 87.

fitting condition for obtaining neat soap of any of the whole range of possible fatty acid concentrations.

It is known that a coarse fit results in a large layer of neat containing more fatty acids than a fine fit, which, in turn, produces a large quantity of soap dissolved in the niger, and a small layer of neat soap which also contains less fatty acids. The problem of good pan yields, the elimination of dark nigers, and the production of a neat soap with low salt content and of good consistency are the biggest problems of the soapmaker. It is therefore of great interest that Wigner's 66% rule gives a glimpse into the quantitative aspects of neat – niger separation and even provides the means for regulating the process.
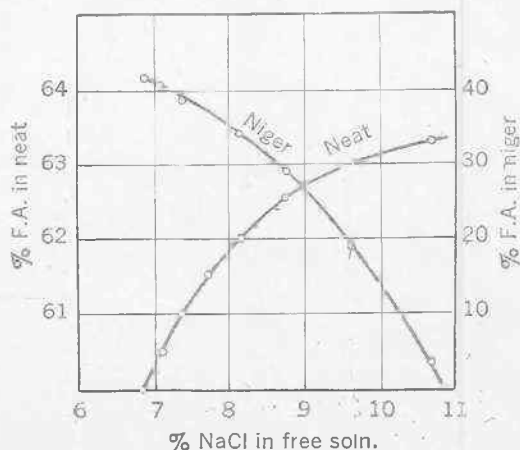
Fig. V-1. Diagram showing relation between fatty acid content in neat or niger and salt content in free solution.[59]

The amount of niger as a fraction of the whole mass in the pan can be calculated when the contents of fatty acids are known for (a) the total mass, (b) the resulting neat soap, and (c) the niger. This amount can be calculated from:

$$\text{Amount of niger} = \frac{\%\ \text{FA in neat soap} - \%\ \text{FA in total mass}}{\%\ \text{FA in neat soap} - \%\ \text{FA in niger}}$$

The following quantitative investigation was carried out by fitting a curd of the same fat charge as investigated in Table V-8 containing 55% fatty acid, 1.45% salt, and 12% salt in the free solution. In this case, the curd just described was diluted in seven consecutive stages and the percentages of salt in free solution calculated for the respective stages. The corresponding values for per cent fatty acid in the neat soap and in the niger were deducted from the chart in Fig. V-1 by drawing the vertical line for each value of "NaCl in

free solution." The percentage of niger in the total mass was then calculated by using the formula in this section. The results are given in Table V-8.

The table illustrates almost everything that may be of interest for the soapmaker in connection with the fitting process as outlined by Wigner and his 66% rule. As more and more water is added gradually to the curd, the amount of free solution increases. The amount of fatty acid in the total mass of curd diminishes, and so does the percentage of salt. The percentage of salt in the free solution diminishes as well and, at the same time, the coarse fit, as shown on the trowel, changes gradually into a finer one. This is accompanied by a steady growth of the lower layer and by an increasing portion of the total fatty acids being dissolved in the niger. The ever diminishing layer of neat soap becomes, in the meantime, gradually less concentrated in regard to fatty acids.

TABLE V-8

FITTING STAGES BEGINNING WITH A CURD WITH 58% FA, 1.45% SALT IN TOTAL MASS, 12% FREE SOLUTION, AND 12% SALT IN THE FREE SOLUTION[59]

FA in total mass, %	NaCl in free soln., %	FA in neat soap, %	FA in niger, %	Niger in total mass, %	Total FA in niger, %	Type of fit	NaCl in total mass, %	Free soln. in total mass, %
56.35	9.65	63	18.5	15.2	4.8	Coarse	1.41	15
55.52	8.75	62.5	28.5	20.6	9.9	—	1.39	16.6
54.88	8.15	62	33.5	25.2	14.6	—	1.37	17.8
54.34	7.70	61.5	36.5	28.8	18.1	Medium	1.35	18.85
53.89	7.35	61	38.5	32.0	21.3	—	1.34	19.75
53.55	7.10	60.5	40.3	34.4	24.0	—	1.331	20.4
53.18	6.85	60	41.5	36.8	26.4	Fine	1.33	21.2

Never throughout the discussions of the results of his interesting experiments and of the 66% rule derived therefrom does Wigner mention the phase rule. But it must be clear that when the validity of the 66% rule will finally be proved this will have to be done on the basis of the phase rule. It appears to us that Wigner's main purpose, to provide a working hypothesis for easy calculation in experimental and practical soapboiling, was achieved. It will be seen in later chapters (cf. Volume II) how easy it becomes to experiment with various fat charges, to change boiling conditions at will and to obtain predetermined results. Wigner's conception of a soap as composed of two components, the one the pure and "electrolyte free soap hydrate containing 66% fatty acid," and the other, the "free solution containing the total amount of electrolytes present in the soap," makes it comparatively easy to conduct the soapmaking process in a rational and quantitative manner.

[59] J. H. Wigner, l.c., p. 94, with some additional data of the authors.

(3) The "Limited Fitting Concentration"

In Merklen's nomenclature, the *lye limit concentration* (L.L.C.) was the minimum salt concentration in the lye at which the lye when in equilibrium with a soap layer did not dissolve any traces of soap. Y. Kawakami advanced another characteristic for the exact knowledge of the fitting process. He determined the salt concentration in relation to the total pan content which was the maximum electrolyte concentration at which the neat soap – niger system could still exist without the appearance of the third phase—the lye.

His experiments were similar to those carried out by the McBain school for the determination of phase boundaries in ternary systems (Ch. II, 6a). The
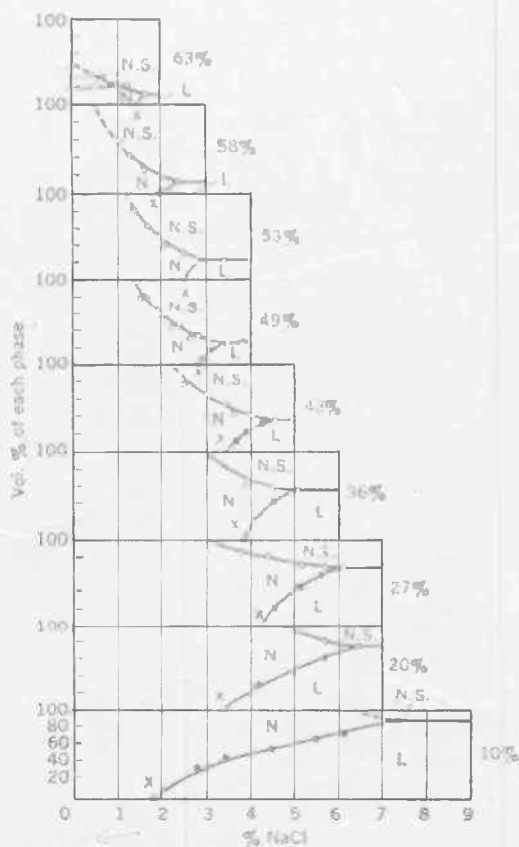
Fig. V-2. Phase volume in the system soap—water—salt for a soap made from 80 parts of beef tallow and 20 parts of coconut oil at nine different soap concentrations.[60] N.S., area of pure neat soap, N, of niger, L, of lye. Point x is L.F.C.

experiments of Kawakami may be called the synthetic determination of phase volume; they acquire special interest because they show the phase behavior of soap made from oils and oil mixtures occurring in the practical soapmaking process.   The powdered soap samples were thoroughly mixed with the salt solutions and introduced into stoppered graduated hard-glass tubes, where they were allowed to settle in a thermostat at 98°C for 24–48 hours, and the volume of neat soap, niger, and lye in equilibrium measured.   There were a series of determinations made on the (commercially) very important mixture of 80 parts of beef tallow and 20 parts of coconut oil.   In Fig. V-2 the[60, 61] phase volumes for soap mixtures at varying salt content in the three-component system soap–water–salt are shown for nine soap concentrations by plotting the phase volume percentages (vertical axis) against per cent of salt in the total mass.
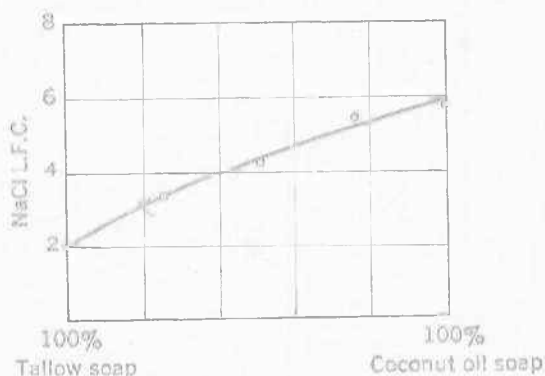
Fig. V-3.   The L.F.C. for tallow–coconut oil–soap mixture in the system soap–water (1 : 1)–salt.[60]

The *limited fitting concentration* will be found on the first vertical line that can be drawn without entering the area of "lye" when trying to do it by starting from the right and proceeding toward the left.   From Fig. V-3 we can derive the L.F.C. for any possible composition between tallow and coconut oil–soap mixture at a soap concentration of 50%.

Fig. V-4 contains the results of measurements carried out with 13 different kinds of soap made from the most familiar oils and fats in practical oil boiling, all soaps having been investigated in 50% solution.

When instead of salt caustic soda was used as electrolyte, it was taken into account by the equivalent reduction concentration of 1 NaOH for 1.15 NaCl.

(4) Separation into Separate Layers of Niger from Neat Soap

Even when the soap and salt concentration of the pan content has been regulated in such a way that, theoretically, the required type of fit should re-

[60] Y. Kawakami, *J. Soc. Chem. Ind. Japan*, Suppl. 898B (1931).
[61] E. I. Better, *Seifen Industrie Kalender*, Delius, Berlin, 185 (1933).
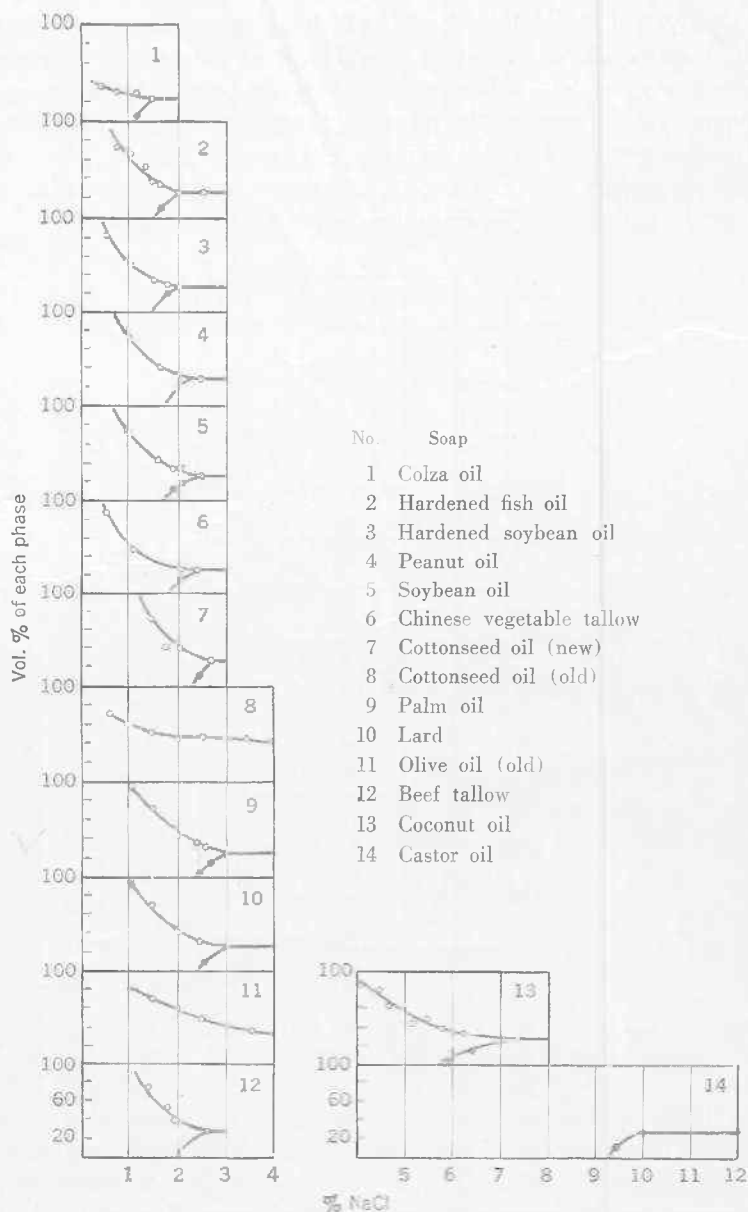
Fig. V-4. Phase volumes in the system soap–water(1 : 1)–salt (variable)
with 14 different soaps.[60] All soaps in 50% solution.

sult, it does not follow that the quantity and composition of the layer after
separation will actually correspond to what is expected by the operator.   For
at this stage of the operation everything depends on the ease, velocity, and

completeness with which the separation of the phases into layers takes place.
It was shown on Ch. V, 2A that no separation at all takes place at certain soap
concentrations because—although the system had become heterogeneous and
two phases, in the sense of the phase rule, are present—the separation into
two layers is prevented by the viscosity of the mass (see Fig. V-5). This is
why the soapmaker when arriving at the final stage of fitting must make cer-
tain that the pan content possesses the desired degree of fluidity.
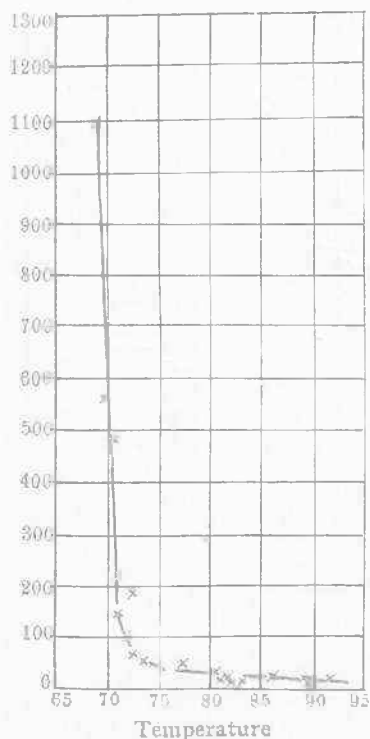
Fig. V-5. Viscosity of neat soap at various temperatures.[63]   Ordinate, time of
falling of 1/2 steel ball through 5 cm. in seconds.

The following experiments were made with a toilet soap charge consist-
ing of beef tallow, coconut oil, and peanut oil (neutralization value of fatty
acids 218, iodine value 39.9).[62]   The saponified, washed, and fitted soap was
taken for settling experiments at a stage at which no settling occurred. 60-cc.
samples were taken from the soap pan, poured into graduated Pyrex glass
tubes with ground-glass stoppers, and introduced into a transparent thermo-
stat held at a temperature of 98 ± 2°C. and the volume of the separated niger

[62] Y. Kawakami, *l.c.*, 181B.
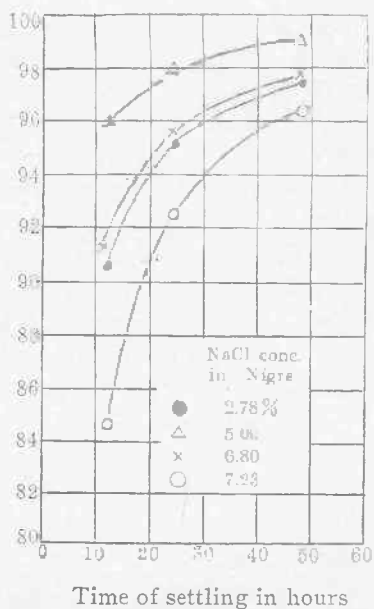
Fig. V-6a. Separation coefficient and settling time for varying NaCl content in the niger.[61] Ordinate, separation coefficient of niger, %.
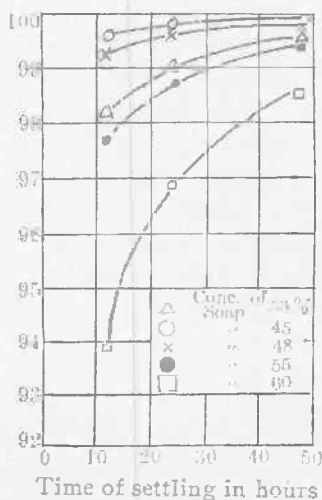
Fig. V-6b. Separation coefficient for varying soap concentrations.[61] Ordinate, separation coefficient of niger, %.

was observed at specific time intervals.   Table V-9 shows the result of these experiments.

The value of these experiments lies in the mathematically defined rule which

TABLE V-9

VOLUME PER CENT OF NIGER SEPARATED FROM NEAT SOAP[52]

Settling time, hrs.	Number of experiments							
	1	2	3	4	5	6	7	8
1	15.0%	25.0%	17.0%	12.5%	26.0%	31.0%	15.0%	20.5%
2	19.5	28.2	23.0	19.5	29.0	33.3	20.6	24.7
4	21.5	29.5	24.2	21.6	32.0	34.2	23.7	27.7
7	22.2	30.8	24.9	22.7	33.0	35.0	24.3	29.5
10	22.7	32.0	25.3	23.2	33.2	35.5	24.5	30.2
20	23.7	33.8	26.1	24.5	33.7	36.5	24.7	32.2
40	24.2	34.5	26.7	25.0	34.3	39.2	25.0	32.6
COMPOSITION OF PAN CONTENT								
Fatty acid, %	51.0	47.7	54.53	50.64	49.18	47.87	51.80	47.3
NaCl, %	1.91	2.48	1.71	1.80	2.17	2.26	2.07	2.18
NaOH, %	0.34	0.51	0.30	0.24	0.30	0.38	0.19	0.31

can be derived. Let V denote the volume per cent of niger separated from the total mass after t hours of settling, and a the volume of niger which would have settled on complete separation. Then the expression $V/a \times 100$ denotes the *separation coefficient of the niger*. Table V-9 permits the graphic calculation of the value of a for each case, and thus it is also possible to calculate the separation coefficient of the niger for each soap composition under investigation and laid down in Table V-10 for five different time intervals.

These results are given in Table V-10 and Figs. V-6a and 6b, which show the separation coefficient plotted against the time of settling in hours, clearly representing the fact that after the first 24 hours of rapid settling there follows a period of at least two days of slow settling, even when temperature is kept constant. This does not apply to commercial work, even with large pans (see Chapter VI-2).

TABLE V-10

SEPARATION COEFFICIENT OF NIGER[2]

Expt. No.	Separation coefficient for settling time of:				
	6	12	24	48	72 hrs.
1	91.2%	95.6%	97.8%	98.9%	99.3%
2	90.4	95.2	97.6	98.8	99.2
3	92.5	96.3	98.1	99.1	99.4
4	89.7	94.8	97.4	98.7	99.4
5	94.7	97.3	98.7	99.3	99.6
6	94.3	97.1	98.6	99.3	99.5
7	95.4	92.6	96.3	98.1	98.8
8	90.0	94.9	97.5	98.7	99.2
Av.	*91.0 ± 2.0*	*95.5 ± 1.0*	*97.7 ± 0.5*	*98.9 ± 0.3*	*99.3 ± 0.2*

Another equation which seems to be thoroughly satisfied by the experimental facts combines mathematically the values a, V, and t by stating that

$$(a-V)\,t = b$$

where b, like a, is a constant that depends only on the concentrations of the soap and electrolyte at fitting.

In order to examine how the separation of niger depends on the concentration of the soap when the condition of salting-out is kept constant, the following tests were made. Dry powdered sodium soap was prepared from 80% beef tallow and 20% coconut oil and mixed with NaCl solution and water in a graduated Pyrex tube in various proportions in order to have, in all cases, approximately the same type of fit, and the contents of the glass tube were settled as above. Volume per cent of niger separated was measured against time (Table V-11). The coefficient of separation on niger is plotted against settling time in Figs. V-6a and 6b.

TABLE V-11

VOLUME PER CENT OF NIGER SEPARATED FROM VARIOUS CONCENTRATIONS OF
SOAP UNDER STANDARD CONDITIONS[6]

Settling time, hrs.	Soap concentration				
	45%	48%	53%	55%	60%
1	50.0%	—	—	—	—
2	51.7	40%	30%	29.5%	10%
3	52.5	42	32	30.1	12
4.5	53.3	43	32.5	30.9	13
7	53.3	43	33	31.4	14
22	53.3	43	33.8	32.5	15
46	53.3	43	34	33.3	15.5
NaCl concn.	3.2	2.9	2.5	2.3	1.8
% NaCl in free soln.	10.1	10.7	12.6	13.8	20.0

These experiments show that the best coefficient of separation is obtained when the concentration of the soap is lowest. But when experiments were made by keeping the soap concentration constant and only electrolyte concentration was varied in order to obtain changing degrees of coarseness of the fit, the results indicated clearly that too coarse a fit retards the separation of the niger, owing to the very high viscosity of the neat soap, while a finer fit also retards it because the difference in specific gravity between the neat soap and niger is too small.
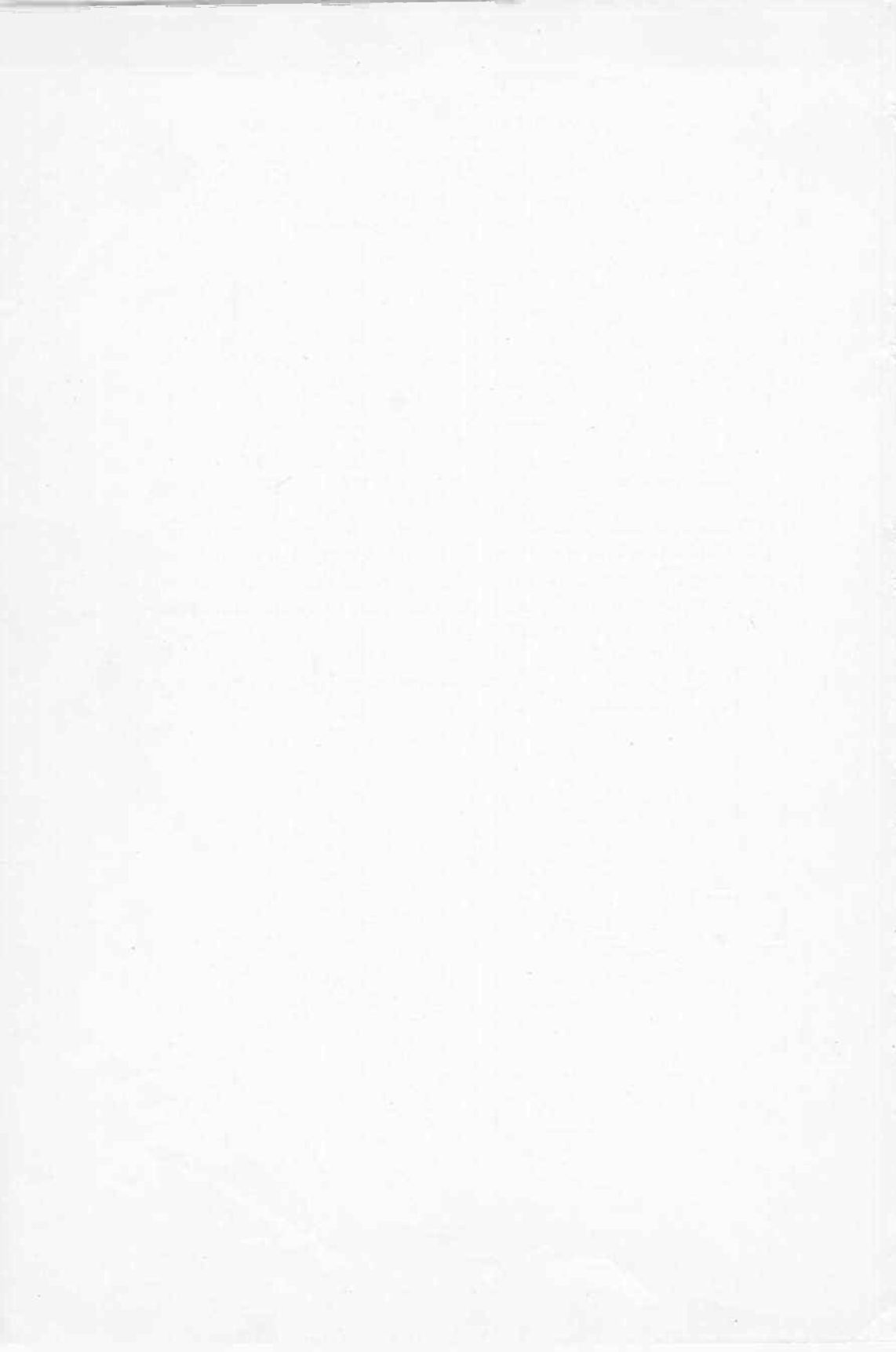
PHYSICAL AND CHEMICAL PROPERTIES OF SOAP AND SOAP PHASES AND THEIR INFLUENCE ON PRACTICAL SOAP PROCESSES

(1) Change of Viscosity of Neat Soap with Temperature

This is a very important factor for an understanding of settling conditions and, accordingly, the results of an investigation carried out by Phipps[63] are of interest. The temperature viscosity curve in Fig. V-5 shows that below 75°C. the viscosity of neat soap increases rapidly and, therefore, practically no separation of niger from the neat soap can be expected below this temperature level.

(2) Influence of Size and Shape of the Soap-Boiling Pan on Settling of Neat Soap

Guided by the principle that niger cannot settle unless the temperature of the soap in the pan is not kept from cooling beyond a certain limit, Webb[64] studied the relationship between pan form and size and the maximum settling time which could be allowed for each type of pan. He found that the rapidity with which the soap mass cools down depends on the cooling surface at the disposal of a given unit of soap mass. The larger the surface and the smaller the quantity of soap that is held in the pan, the more rapidly will the soap cool down. The quotient of the effective cooling surface and the effective volume of the pan is called by Webb the "pan factor," and he stated that the smaller this factor the larger the period of settling which may still be effective. That is, with a small pan factor the temperature will drop slower than with a large one. Thus, e.g., with a pan factor of 1.319 the temperature of the

[63] H. E. Phipps, *Coll. Sym. Mon.*, 5, p. 259, through Kawakami, *l.c.*
[64] E. T. Webb, *Soap and Glycerine Manufacture*, Davis, London, 1927.

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mass will cool below the minimum temperature (65°C., in the opinion of Webb) in 97.3 hours against 38.5 hours with a pan factor of 3.334. This would mean that a large pan must be more suitable for settling than a small pan. In this calculation, however, only the factor of rapidity with which the cooling takes place was taken into consideration, whereas, as mentioned above, the settling rate, and consequently the height through which the niger has to sink, must also be taken into account. Accordingly, not only the pan factor, but also the height of the pan, is of importance and it will be found that the best results in settling will be given by pans possessing a sufficiently low pan factor (which will consequently hold the temperature for a satisfactory period) and which, at the same time, is sufficiently shallow so that the niger will not have to sink through too deep a layer.

Lascaray[65] offers a corrected calculation for the longest allowable settling period. We will reproduce it here as a good example of a thermal calculation, in order to indicate the way in which such problems must be approached.

The total heat contained in the soap charge is equal to the weight of the charge (which may also be represented by volume, V) multiplied by the temperature, T, and by the specific heat of the soap (0.7 for 50% soap solution). The total heat content of 1000 lbs. of the soap at boiling temperature is $1000\ V \times 100 \times 0.7$ Cal. The minimum temperature of soap settling, in our opinion, is 75° C., and the pan content will have to dissipate $1000\ V \times (100-75) \times 0.7$ Cal. in order to permit the temperature of the total pan content to fall to 75° C. This loss of heat, however, takes place only through the effective cooling surface of the pan (F square meters). It is known that, under the conditions prevailing in soap factories, soap pans, when properly lagged, lose 125 Cal. per hour per square meter (Webb proposes 303.8 Cal., which was found by Lascaray to be exceedingly high). The problem is now reduced to the question of how long it will take until $1000\ V \times (100-75) \times 0.7$ Cal. would be lost by radiation through the area F. This period is given by the following expression:

$$\tau = \frac{1000\ V\,(100-75)\,0.7}{125\ F} = \frac{V}{F} \times \frac{1000 \times 0.7\,(100-75)}{125} = 140\ \frac{V}{F}$$

The time during which the temperature of the pan contents cools down to 75°C. can be expressed by multiplying the quotient V/F (identical to the pan factor of Webb) by a constant.

After the necessary cooling period has thus been established, we have yet to see whether that time will be sufficient to allow even the smallest drop of the niger to sink from the surface of the pan contents to the surface of the lower layer. This will depend on the rate of separation v. The value of v is expressed in terms of height per unit time and, consequently, the time v necessary for the smallest droplet of niger to reach the bottom after sinking through the height H of the neat layer, is:

$$\delta = k\,(H/v)$$

where k is a constant dependent on the volume ratio of neat soap and niger. It is obvious that τ must not be smaller than v. Consequently when $\tau = \delta$, the equation becomes:

$$140\ \frac{V}{F} = k\ \frac{H}{v} \qquad \text{and} \qquad \frac{140}{k} = H\ \frac{F}{v} = \text{height}\frac{\text{surface area}}{\text{volume}}$$

[65] L. Lascaray, *Seifensieder Ztg.*, 65, 901 (1938),

The expression H (F, v) has been called by Lascaray the *pan coefficient*, and this new factor fully characterizes the pan as to the completeness with which all particles of the niger can separate from the neat. The smaller the *pan coefficient* the more complete will be the separation of the niger. But when the complete meaning of the pan coefficient is taken into consideration it is clear that the shape and not the size of the pan is of ultimate importance. At the same rate of settling, separation will be completed sooner in a shallow pan of large diameter than in a high of narrow diameter. These conditions are valid only when the pan is well lagged and covered at the top.

The following are general rules regarding the shape of the pan: (*a*) rectangular pans of square area have settling efficiency equal to that of pans of cylindrical shape when the ratio of height to diameter or width is equal in both; (*b*) rectangular pans of nonsquare area are less efficient and become

TABLE VI-1

SOME VALUES OF τ FOR CYLINDRICAL PANS[65]

V. useful volume, cu. meter	τ, max. effective settling time, hrs.
1	13
5	43
10	55
25	74
50	95
100	117

even less so with increasing difference between the sides; (*c*) conical pans are better than cylindrical ones; however, they become less efficient when the quotient height radius becomes less than 0.5; (*d*) pans in the shape of a truncated cone have a medium settling efficiency as shown by conical and cylindrical pans, respectively.

(3) Variation in Composition of Niger Owing to Fractional Salting-Out

It was shown on the phase diagrams for various pure soaps (Chap. IV) and also by differences in the limit of lye concentrations for various soaps that low molecular weight fatty acid soaps are salted-out less readily than those of high molecular weight.

It was to be expected that, in the distribution of low molecular fatty acid between neat soap and niger, the latter will tend to be richer in this part of the fat charge.

Figs. VI-1 and VI-2 contain the results of experiments[66] made by fitting

[66] Y. Kawakami, *l.c.*, p. 94B.

soap containing varying proportions of coconut oil. The soap concentration
of the pan contents, in this experiment, was held at the constant concentration
of 50% while the salt concentration had to be increased according to the
limited-fitting-concentration of the soap composition in order to receive more
or less the same type of fit. The neutralization value is the measure of the
contents of the particular soap on low molecular weight fatty acids, and the
higher the neutralization value the more low molecular fatty acids are con-
tained in the soap. It can be seen that the niger, in fact, always contains more
low molecular fatty acids than the neat soap.
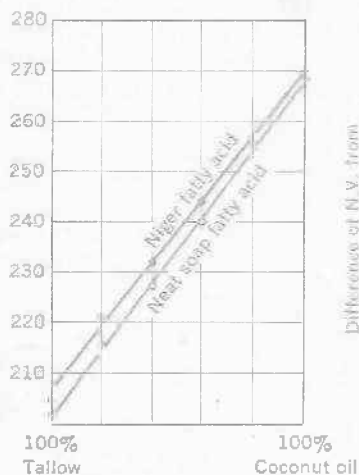
Fig. VI-1. Neutralization value of
fatty acids (ordinate) in the neat
soap and in the niger with various
soap compositions, but at the same
type of fit.[66]
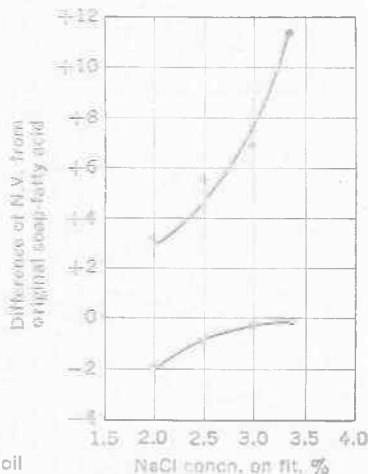
Fig. VI-2. Neutralization value of
fatty acids in the neat soap and in
the niger with one soap, but at vari-
ous degrees of fit.[66]

In another experiment the fractional salting-out of low molecular weight
fatty acids was studied on a pan charge of 80% tallow–20% coconut oil,
when fitted with various salt concentrations to different types of fit. The
results show that the coarser the fit, the more fractionation takes place and
the richer is the niger in low molecular weight fatty acids.

When investigating how many times the niger can be used for subse-
quent boils without fractionating the charge to such an extent as to change the
composition of the charge altogether, it was found that after four uses of the
niger no more fractionation was taking place. During this time the neutraliza-
tion value of the fatty acids in the niger increased from 219 to 223.

Table VI-1A shows the results of an experiment performed on a charge of
80% tallow–20% coconut oil with the view to attaining the highest possible

degree of fractionation between the fatty acid component by numerous subsequent fractional salting-out in the system neat soap–niger. The degree of fractionation is not high, but it must be borne in mind that, nevertheless, there exists, in practice, some variation in neutralization values for the same pan charge. This is particularly important for the analytical chemist, for whom this value constitutes an important figure. A difference of 5 units in the neutralization value indicates an increase or decrease of approximately 2% coconut oil. In the case of fractionation from a neat soap with a neutralization value of 216.6 to 211.5, this means that, whereas the soap contained 20% coconut oil at the beginning, it contained only 17.9% at the end of the fractionation process.

TABLE VI-1A
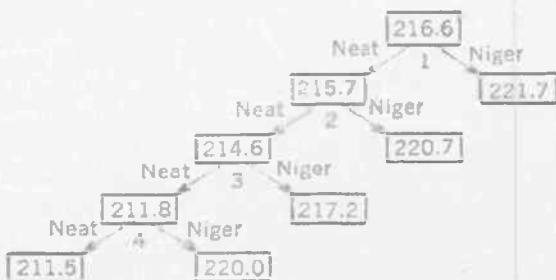
(4) Distribution of Electrolyte between Curd and Lye or Neat Soap and Niger

Many attempts have been made to find mathematical expressions for the relation between the quantity of electrolytes contained in the layers of the pan at equilibrium. It is obvious that the soap layers, curd or neat soap, always contain less electrolytes than the lower layer, whether lye or niger. Until the present there has been no rule of general validity by which we could predict from the knowledge of the electrolyte concentration in the lye the exact content of the salted-out soap. However, as mentioned before, some authors tried to advance some rules with regard to such correlations.

Goldschmidt[67] found that the equilibria between the strong lye and its curd, in Merklen's experiment with poppyseed oil and lard, satisfy the requirements of the Freundlich adsorption isotherm, and he states that, in this equilibrium, the concentration of salt in the lye was equal to 1.85 times the concentration of the salt in the pure soap to the power of 4.34. For instance, we will find in Table V-2 that the strong lye contained 15.4% NaCl, and that

[67] F. Goldschmidt. *Seifenfabr.*, *31*, 225 (1911). E. L. Lederer, *Kolloidchemie der Seifen*, Steinkopff, Dresden and Leipzig, 1932, p. 358.

the curd contained 1.16% NaCl and 71% pure soap; consequently, there was 1.63% NaCl in the pure soap, so that:

$$15.4 = \text{constant} \times 1.63^n$$

Goldschmidt proposes the values: constant = 1.85 and $n = 4.34$; in this case $15.4 = 1.85 \times 1.63^{4.34}$, which would correspond to the values found by Merklen.

It can be shown, however, that this equation does not satisfy all the experimental data available, and workers like Ubbelohde, Baetz, and Thoerl[68, 69] conclude from Merklen's data that there is generally about 11 times more electrolyte in the lye than in the curd in equilibrium. The same authors propose, for the system neat soap–niger–lye, a distribution in the proportion of 1:7:9, but it is clear from a scientific approach to their experimental data that this proportion can be regarded as only a very rough estimate. The last mentioned authors distinguish between a "natural" system of fitting and the "fitting system" as such. The first system occurs when small portions of electrolyte are added to a batch of homogeneous soap solution until the proper type of fit is produced. This "natural" system produces nigers with small soap contents only. The "fitting system" proper is similar to actual practice, where portions of water are added to an "open" curd until the pan content is sufficiently "closed" to supply the necessary fit.

Results of Thoerl show that in this last type of fitting the electrolyte content of the neat soap is increasing and that of the niger is decreasing when the fitting lye concentration is gradually decreased. Lederer[70] explains that it is difficult to give any rule which would express the interrelation between the electrolyte contents of neat soap and niger. He further maintains that this difficulty induced Merklen to relate the analysis of the neat soap not directly to the composition of the niger, but to the composition of the "fitting lye," which separates from it on cooling.

In Chapter V, Section 2, experiments carried out by Wigner, and the so-called 66% rule are explained. When trying to check this rule against experimental data of others, we found that the rule holds good to a certain restricted degree, especially at medium soap concentration in curd and neat soaps: mainly when the soap charge does not contain too large a quantity of low molecular fatty acids (coconut oil) or fatty acids containing hydroxy groups or oxidized fats; in short, in cases where the "lye limit concentration" of the soap is not too high.

Wigner, in fact, never mentions the exact composition of the soaps used in connection with this experiment and thus we were not able to check his

68 Ubbelohde and Baetz, *Thesis*, Karlsruhe, 1918.

69 *Idem*.

70 E. L. Lederer, *Kolloidchemie der Seifen*, Steinkopff, Dresden and Leipzig, 1932, p. 363.

TABLE VI-2

TALLOW SOAP IN THE "NATURAL" AND "FITTING" SYSTEMS[69]
ELECTROLYTE: NaOH WITH TRACES OF Na_2CO_3

System	Per cent fatty acids		Electrolyte red. concn., %						Total electrolyte content		
	Niger	Neat	Lye		Niger		Neat		Lye	Niger	Neat
			NaOH	Na_2CO_3	NaOH	Na_2CO_3	NaOH				
Natural System											
Lye–niger–neat	10.30	61.30	5.57	0.29	4.57	0.24	0.45	0.15	5.86	4.81	0.60
	10.40	60.40	5.84	0.11	4.52	0.18	0.65	0.08	5.95	4.70	0.73
	10.40	59.10	5.68	0.31	4.54	0.22	0.25	0.24	6.00	4.76	0.49
	10.75	59.00	5.86	0.18	4.42	0.19	0.50	0.09	6.04	4.61	0.59
	?	60.7	6.10	0.25	?	?	0.45	0.09	6.35	?	0.54
	9.6	60.8	6.24	0.16	5.15	0.18	0.37	0.17	7.42	—	0.64
Lye–neat	—	61.7	7.25	0.17	—	—	0.57	0.07	7.42	—	0.64
	—	61.4	7.70	0.28	—	—	0.69	0.13	7.98	—	0.82
	—	63.4	9.40	0.34	—	—	0.59	0.23	9.74	—	0.82
Fitting System[69]											
Lye–niger–neat	10.4	60.4	5.84	0.11	4.52	0.18	0.65	0.08	5.95	4.70	0.73
Lye–neat	18.4	59.8	—	—	3.90	0.18	0.54	0.07	—	4.08	0.61
	22.0	58.0	—	—	3.35	0.10	0.48	0.05	—	3.45	0.53
	22.75	54.7	—	—	3.12	0.12	1.10	0.15	—	3.24	1.25
	24.6	41.4	—	—	2.72	0.15	1.32	0.20	—	2.87	1.52
	25.4	41.0	—	—	2.65	0.15	1.50	0.08	—	2.80	1.58
	26.7	39.8	—	—	2.40	0.13	1.58	0.03	—	2.53	1.61
Niger	34.9	—	—	—	1.72	0.24	—	—	—	1.96	—

experiments. His awareness of the limitations of his rule is expressed in one instance (*l.c.* p. 40) when he shows that soap of more satisfactory hardness is

TABLE VI-3

TALLOW SOAP IN THE "NATURAL" SYSTEM.[8]   ELECTROLYTE: NaCl

System	Per cent fatty acids		Free electrolyte in % NaCl			Reduced concn. in % NaOH			Remarks
	Niger	Neat	Lye	Niger	Neat	Lye	Niger	Neat	
Lye–niger	5.6	—	5.54	4.72	—	4.82	4.11	—	
Lye–niger–neat	5.4	—	5.59	4.30	—	4.86	3.74	—	Lye–niger
	(24.3?)	57.1	6.29	5.86	0.67	5.47	5.10	0.58	
	5.8	57.1	6.32	5.67	0.61	5.50	4.93	0.53	
Lye–neat	—	60.1	6.39	—	0.67	5.56	—	0.58	Lye–neat
	—	59.8	6.60	—	0.76	5.74	—	0.66	
	—	61.6	10.68	—	1.14	9.29	—	0.99	
	—	60.0	12.66	—	1.46	11.01	—	1.27	

produced when peanut oil soap is boiled on high concentration lyes. The salt and fatty acid content of this soap boiled on a lye of 17% salt content does not come within the scope of his 66% rule, since the soap seems to contain, in this case, a hydrate with 70% fatty acid. This experiment made it obvious that the relative validity of the 66% rule is restricted to some small area of the phase diagram of certain soaps. However, it seems that the area covered by this rule encompasses to the most important areas, from the point of view of the practical soapmaking process, of graining and fitting.

Complete information will be available only when phase diagrams for all practically important fat mixtures at all temperatures are prepared, but until that time it seems that, as a working hypothesis, the 66% rule should be accepted tentatively and employed for the badly needed practical control of the soapmaking processes in the restricted sense as outlined above.

Exactly what does the 66% rule of Wigner imply? It says that, when a given pan contains, say, 100 kg. of mixed soap and lye in which the soap is totally salted-out (this mixture consisting of: a, total soap; b, total water; c, total salt; the glycerine content is omitted for the sake of simplicity), then this mass will separate into curd and lye, with the curd containing the total soap, part of the salt and part of the water; the lye will contain the balance.

In accordance with the 66% rule the curd contains the pure 66% soap hydrate plus the free solution. The amount of 66% pure soap hydrate can be calculated when the total fatty acid content of the curd (which, in this case, is the weight of fatty acid present in the whole system) is multiplied by the constant 1.515. The free solution is equal to the weight of the curd minus the weight of the 66% soap hydrate. Another assumption of the 66% rule is that the free solution in the curd contains the same percentage of salt as the spent lye from which the curd has separated. When all these assumptions are taken into consideration the quantity of salt present in the curd can be expressed as follows (all quantities in kilograms):

$$\text{Salt in curd} = \frac{\text{Salt in lye}}{\text{lye}} \, (\text{curd} - 1.515 \text{ FA total})$$

If the equation is multiplied by 100/curd, then it becomes:

$$100 \, \frac{\text{salt in curd}}{\text{curd}} = \frac{\text{salt in lye}}{\text{lye}} - \frac{100 \times \text{salt in lye}}{\text{Lye}} \times \frac{1.515 \text{ FA total}}{\text{curd}}$$

since: $\dfrac{100 \times \text{salt in curd}}{\text{curd}} = \%$ salt in curd

and: $\dfrac{100 \times \text{salt in lye}}{\text{lye}} = \%$ salt in lye

$$\% \text{ salt in curd} = \% \text{ salt in lye} - \% \text{ salt in lye} \times \frac{\% \text{ FA in curd}}{100}$$

and, consequently, we arrive at the equation formulated by Wigner:

$$\frac{\% \text{ salt in curd}}{\% \text{ salt in lye}} = 1 - \frac{\% \text{ FA in curd}}{100} \times 1.515$$

This equation expresses that to each pair of values of FA in curd and NaCl in lye there is only one value of salt in curd and that it is possible to calculate the quantity of salt in the curd when the concentration of salt in the lye and of the fatty acid in the curd is known.

There is another implication in the 66% rule that can be seen more clearly from the nomogram published[26] by Wigner (Fig. VI-3). It will be seen that, by starting from the point of 50% FA in soap and by drawing a line through, say, the 2% point for NaCl in soap, the point met on the third vertical will be in the vicinity of 8% NaCl in the lye. 1% NaCl in the soap will correspond to about 4% in the lye. That means a proportion of 1:4 in electrolyte content between soap and lye. With a curd containing 55% FA the line through 1% salt in the curd will show that it is in equilibrium with a lye containing 6% salt, thus giving evidence for a proportion of 1:6. According to the nomogram, a soap with 60% FA has an electrolyte relation of about 11, and with 63% FA in the curd this relation even goes beyond 1:20. This means that, in the system curd–lye with a curd low in fatty acid, the curd will be much more preferred in the distribution of electrolyte between lye and curd than with a curd high in fatty acid content. Curds high in fatty acid content accordingly have much lower electrolyte concentrations than curds with low fatty acid content.

This tendency can be seen from the various tables above, where, in the neat soap–niger system, concentrated curds are in equilibrium with niger in which the free solution is more concentrated with regard to salt than niger in equilibrium with neat soap containing less fatty acids. In this respect, there is qualitative agreement between Wigner's results and the earlier investigations of Ubbelohde and Thoerl, who found that, in the "fitting" system (contrary to their "natural" system), where fitting is carried out by adding water to an open curd, high fatty acid content curds contain less electrolytes and are separated from nigers which are more concentrated in salt.

(5) Distribution of Glycerine between Curd and Lye or Neat Soap and Niger

The distribution of glycerine was studied by Kawakami by dissolving 3–5 g. pure soap of various compositions, adding 0.1–1.5 ml. of glycerine and 10 ml. of an 8–20% sodium chloride solution, mixing the components, and allowing them to separate for 4–8 hours. After complete separation had taken place, the layers were analyzed for glycerine. It was found that the distribution of glycerine in curd soap and lye satisfies the Freundlich adsorp-
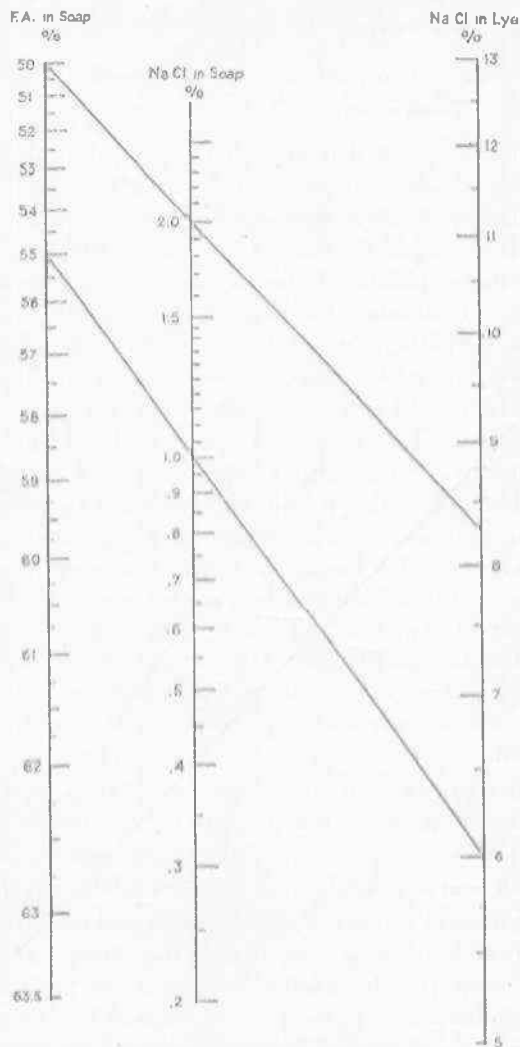
Fig. VI-3. Nomogram calculating salt in soap and in free solution.[56]

tion isotherm. The author derives from his experimental data the following equation for the soaps investigated:

Soap	$\log y$
Sodium palmitate	$0.79 \log x - 0.31$
Tallow	$0.82 \log x - 0.44$
Coconut oil	$0.80 \log x - 0.41$
Cottonseed oil	$0.63 \log x - 0.39$
Castor oil	$0.75 \log x - 0.13$
Rosin	$0.62 \log x - 0.17$

where y is per cent concentration of glycerine in curd soaps, expressed in 100 parts of pure curd soap; and x is a 10% concentration of glycerine in lye, expressed in 100 parts of water in lye.

In order to determine roughly how many times salting-out must be repeated to yield a reasonable recovery of glycerine, we assume that the fat charge is one unit; then roughly 1.5 units of curd soap will be obtained. If the quantity of lye used is a and the glycerine content in the charge is σ_1,

$$\sigma_1 = \frac{\text{Mol. wt. glycerine} \times 100}{3 \text{ mol. wt. KOH} \times 1000} \times \text{Ester value,}$$

or, by direct glycerine determination in the charge, when y_1 is the per cent glycerine in the pure curd soap and x_1 is the per cent glycerine in the lye after the first graining-out, then:

$$\sigma_1 = 1.5 \ y_1 + a_1 x_1$$

In this equation there are two unknown quantities. As the required second equation we can, however, use the isothermic equation related to the fat charge. In the case of coconut oil soap this will be:

$$\log y_1 = 0.8 \log x_1 - 0.41.$$

On the second salting-out the total glycerine content of the charge will be 1.5 y_1, representing the glycerine left in the curd after the first graining. Consequently:

$$1.5 \ y_2 + a_2 x_2 = 1.5 \ y_1$$

and:

$$\log y_2 = 0.8 \log x_2 - 0.41$$

from which the value of x_2 can be calculated, and thus the contents of x_n of the lye on glycerine from any nth salting-out can be calculated from the equations:

$$1.5 \ y_n + a_n x_n = 1.5 \ y_{n-1}$$
$$\log y_n = 0.8 \log x_n - 0.41.$$

Solving these equations consecutively, we can determine the number of times salting-out must be accomplished in order to give a certain glycerine yield.

As a practical experiment, 80 kg. of tallow and 20 kg. of coconut oil were saponified and salted-out four times. In this case, the charge contained 10.9% glycerine; consequently:

$$1.5 \ y_1 + ax_1 = 10.9$$
$$\log y = 0.82 \log x - 0.43.$$

Graphs have been constructed from these two equations and the values read

for each consecutive salting-out. At the same time, the quantity of lye in kilograms and the content of glycerine in soap and in lye were analytically checked, and the calculated values were thus verified by experiment. (Table VI-4.)

TABLE VI-4

GLYCERINE CONTENT IN SOAP AND LYE[71]

No. of times salted-out	Lye kg.	w	Glycerine in lye, %		Glycerine in soap, %	
			Found	Calc.	Found	Calc.
1	99.5	1.0	7.25	7.6	2.10	2.4
2	74.8	0.75	2.54	2.8	0.92	1.0
3	94.4	0.6	1.33	1.2	0.52	0.6
4	67.1	0.7	0.57	0.6	0.25	0.4

However, there is a simpler approach to the question of distribution of glycerine between curd and lye. It can be stated that glycerine is distributed between two layers approximately in the same relation as the water present in both. This can be expressed by the following relation:

$$\frac{\text{Water in curd}}{\text{Water in lye}} = \frac{\text{glycerine in curd}}{\text{glycerine in lye}}$$

from which it is obvious that in one graining-out operation the lye will carry away relatively more glycerine when the water content of the curd is lower. In other words, it is very important to produce curds high in fat content. On the other hand, the lye will carry more glycerine when the amount of lye, as expressed in relation to the quantity of fatty acids involved in the operation, is as high as possible. Of course, there is a limit to the amount of water that can be added to the lye, since this also involves dilution of the glycerine, and dilution beyond a certain maximum limit makes the process of evaporation too costly.

This correlation between the fatty acid content in the curd, and the quantity of lye in relation to the quantity of fatty acids involved was taken into consideration by Wigner, who constructed a very practical nomogram[72] for the quick determination of the fraction of total glycerine removed by the lye.

Part (a) of the nomogram (Fig. VI-4) is applied as follows: If, for instance, such quantities of water and salt are added to a soap charge from 100 kg. of fats that the 95 kg. of fatty acids present are separated as an acid containing 60% fat on 70 kg. of lye, then 1 unit of fat yields 0.736 unit of lye and, as a result, we shall have removed about 54% of the total glycerine present in the charge with the first change.

[71] Y. Kawakami, *J. Soc. Chem. Ind. Japan*, Suppl. 186B (1931).
[72] J. H. Wigner, *Soap Perfumery and Cosmetics*, **12**, 231 (1939).

Part (b) of the nomogram is applied as follows: Having established what part of the total glycerine can be removed by one change, the nomogram enables us to calculate the number of changes necessary to reach a certain percentage of total recovery. With 54% of the glycerine removed in the first change, we shall need 3 changes to reach a 90% total yield.

The glycerine content of a fat charge depends on the kind of fatty acid in the composition and also on the free fatty acid content. Fats containing fatty acids of short molecular chain, like coconut oil, contain more glycerine than those which are composed mainly of higher fatty acids. Again, a fat charge containing only neutral fat will contain more glycerine than a fat charge composed of the same fats, but containing free fatty acids.
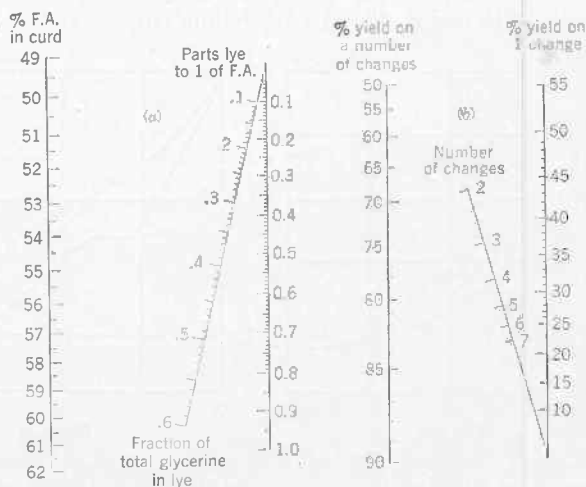
Fig. VI-4. (a) Distribution of glycerine between curd and lye. (b) Effect of several washes.[75]

(6) Solidification of a Liquid Soap Gel by Cooling

We have already touched upon this problem several times and explained that McBain and his school, and also Thiessen, regarded the temperature at which the liquid anisotropic phase neat soap shows the first sign of white curd formation as characteristic data for each kind of soap. It will be remembered that the T_c curves played an important role in the determination of phase diagrams.

Still earlier, M. H. Fischer[73] observed the process of cooling of soap systems and laid special emphasis on the importance of the temperature point at which the solidifying system produces a certain quantity of heat, thus making

[75] M. H. Fischer, Koll. Zeitschr., 46, 359 (1928).

it possible to detect the exact point at which the solidifying actually takes place. The actual solidifying point can also be recognized through the change in the electric conductance of the system. Experiments by Fischer have shown the most interesting fact that all three methods of observation—visual, electrical, and thermal—gave the same result. The solidifying point of a soap system can thus be determined very nearly in the same manner outlined for the solidifying point of mixtures of fatty acids (see titer test, Chapter XXXVIII, Section 13). Figs. VI-5[73] and VI-6[74] show typical cooling curves for four different soap systems.

Fig. VI-6 shows that the time versus logarithm of the temperature during cooling is approximately a straight line, with a break representing the solidification heat which will be generated. In the case of sodium stearate the break occurs at 52°C. and, in the case of sodium laurate, at 11.5°C.
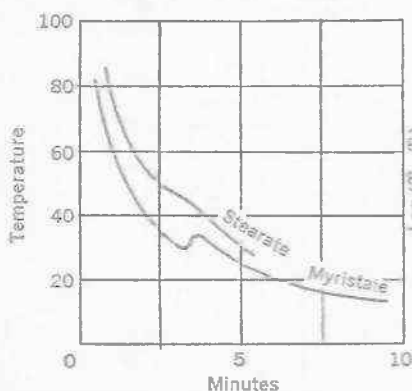
Fig. VI-5. Cooling curves of 15% so-   Fig. VI-6. Cooling curve from
      dium soap solutions.[73]   Fig. VI-5 in logarithmic scale.[74]
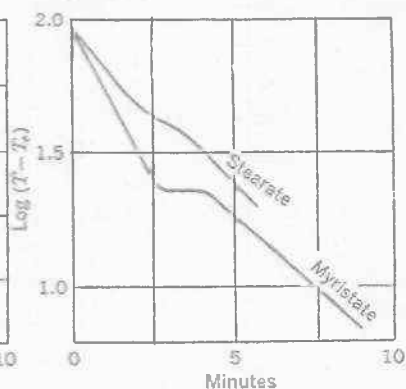
In the definition of McBain, we distinguish between three forms of soap hydrates when: (a) the soap solution is a clear, transparent liquid with viscosities between that of water and values 1000 times as great; (b) the soap gels are clear, transparent solids showing definite elastic properties; (c) the soap curd fibers are more or less opaque white masses. The T_c values of McBain show the transformation boundaries from transparent gel into the phase in which curd fibers appear. Fischer's solidifying point characterized by the appearance of a sudden rise in temperature, as shown in Fig. VI-5, fixes (as pointed out by Lederer) the transformation of a soap solution in an immobilized, but still transparent, soap gel.

Every practical soapmaker will have observed that, when heating soap in any shaped form, the piece will undergo changes, first by becoming trans-

[74] E. L. Lederer, l.c., p. 38.

parent and only later by melting into a shapeless mass. In the other case, when opening a soap-cooling press before the proper cooling period is terminated, we may obtain a plate of soap which will keep its shape fairly well but which is still transparent.

TABLE VI-5

SOLIDIFICATION POINT OF NEAT SOAP[75]

Kind of soap			Fatty acid in soap		Solidif. pt. of neat soap	Av. so-lidif. pt.
			I.v.	M.p.		
Toilet soap base			38.3	37.8	52, 52, 52.6, 53	52.4
Laundry soap base			44.8	35	37.6. 38.4.	38.0
Cottonseed oil			110.3	34.5	32. 33	32.5
Hardened cottonseed oil			69.3	36	33	33
			45.1	42.5	46.3, 45.9	46.1
			27.3	46.5	60, 58.5	59.3
Hardened coconut oil			4.6	26	61.5	61.5
Coconut oil			8.5	24.8	59.5. 59.2. 60	59.6
Coconut oil (80%)-tallow	(20%)		15.5	27	58.2, 59	58.6
(75%)	(25%)		17.0	27.2	59	59
(60%)	(40%)		22	30	56.9, 56.6	56.8
(50%)	(50%)		25.5	34.5	54.5	54.5
(40%)	(60%)		29	39	51.4	51.7
(25%)	(75%)		34	40	51	51
(20%)	(80%)		35.5	40.5	51.6, 51	51.3
Beef tallow			42.6	43	48.1, 48.7, 50	48.9
Hardened fish oil			66.7	37.5	44.7	44.7
			10.2	52.5	66.6, 66	66.3
Hardened soybean oil			57	41.5	47.4, 48	47.7
Soybean oil			125	22	27	27
Palm oil			42.1	43.5	45. 46.5	45.8
Chinese vegetable tallow			28.2	52.5	62	62
Peanut oil			98.5	27	27	27
Sodium palmitate			0	63.6	76.5. 77.5	77
Sodium laurate			0	43.6	72. 73	72.5

(7) Solidification Point of Neat Soap

The solidification point of neat soap was determined by Kawakami[75] by means of the electroconductivity and the differential thermal methods. The data of Kawakami are noteworthy in view of the fact that they were obtained on important soap systems, and because he brought them in interesting relations to the iodine values and melting points of the fatty acids from which the neat soaps were produced. From Table VI-5 the following can be derived. When plotting the solidifying points of the soap against the melting

[75] Y. Kawakami, *l.c.*, 31B (1932).

points of the fatty acids for soap which do not contain low molecular fatty acids, a straight line is obtained which can be expressed as follows:

$$T_s = 1.34\ T_f - 8.5$$

where T_s is the solidifying point of the neat soap, and T_f is the melting point of fatty acids. Soaps containing mixtures of coconut oil and tallow are represented by another straight line and another linear equation. The solidifying point of neat soap can thus be read off from the diagram or calculated when the melting point of the fatty acid composition is known.

(8) Rate of Cooling of Neat Soap

It is important for the soap plant operator to know what cooling interval to allow for complete solidification of the slab or block. In order to find whether a rule exists that expresses the cooling time if other data are known, a series of experiments were carried out with a toilet soap base (15% coconut oil 85% tallow) which had been cooled in differently shaped frames of different sizes. The temperature at the center of the block was measured at each time interval and, at the same time, the room temperature was registered. Table VI-6 gives the experimental data.[75] T_A is the temperature of the soap before cooling started; T_e is the mean room temperature; a is a constant, changing with the size and type of frame material and with the kind of soap; b is the time, in hours, from charging the soap into the frame until the moment the soap starts to cool in the center of the slab.

When T is the temperature of the soap in the center after time t (necessary for cooling), the following equation will hold:

$$t = \frac{\log\ (T_A - T_e) - \log\ (T - T_e) + ab}{a}$$

or:

$$t = \frac{1}{a} \log \left(\frac{T_A - T_e}{T - T_e} \right) + b$$

As a practical example, let $T_e = 18°C.$, $T_A = 80°C.$, and the solidifying point of the neat soap $53°C.$, then $t = (0.248\ a) + b$. a and b, which can be taken from Table VI-6 for each kind of frame.

Table VI-6 gives values for cooling frames of various sizes. However, the above equation holds for cooling in presses as well. Table VI-7 contains values for a and b for cooling pan plates of various sizes. By their use, the cooling time required in cooling presses can be calculated.

(9) Water Absorption by and Drying of Solid Soap Gels

Dry soap, and especially dry soap in powdered form, will absorb water from the air. The rate and degree of water absorption will depend on the

TABLE VI-6

DATA FOR SOAP COOLING IN FRAMES[15]

Expt. No.	Soap temp. before cooling, T	Av. room temp., T_e		b	Frame size
1	80	22.5	0.00398	15	Mild steel frame, 9 ×61×76 cm. Thick-
2	82	25.5	0.00423	15	ness of iron plate 3 mm., No. 1 frame.
3	78.5	26	0.00384	19	
4	80	26	0.00430	20	
5	82	26	0.00453	16	
6	78.5	28.5	0.00394	16	
7	79	28	0.00424	18	
8	80	24	0.00416	18	
9	79.5	26.5	0.00412	18	
10	79.5	29.5	0.00414	16	
11	79.5	19	0.00408	19	
12	79	15	0.00376	18	
13	80.5	12	0.00378	19	
Average			*0.0041*	*17*	
1	81.5	24	0.00780	8.5	Mild steel frame (3 mm. thick), $91×61×$
2	83	27.5	0.00825	10	38 cm., No. 2 frame.
3	82	26.5	0.00715	10	
4	79	30	0.00725	9	
5	82	30	0.00755	8	
6	82.6	30	0.00854	8.5	
7	79	19	0.00800	9.5	
8	79	14.5	0.00735	9.5	
Average			*0.00771*	*9.1*	
1	85	21	0.0165	2.0	Wooden frame (27 mm. thick), 18.5 × 45 ×
2	79	21	0.0159	2.1	20 cm. No. 4 frame.
Average			*0.0226*	*1.8*	
1	75.1	24.1	0.0226	1.8	Wooden frame (27 mm. thick), $18.5 × 45 ×$ 20 cm., No. 4 frame.
1	87.8	15.6	0.026	3.0	Tinplate frame (0.5 mm. thick), $24.5 ×$ 24.5 × 34 cm. No. 5 frame.
1	78	17.5	0.057	1.0	Wooden frame (17.2 mm. thick), 13.7 ×
2	88	16	0.059	1.0	18.3 × 12.5 cm., No. 6 frame.
Average			*0.058*	*1.0*	
1	85.5	17.5	0.078	0.9	Tinplate frame (0.71 mm. thick), 13.7 ×
2	82.5	10.5	0.075	0.9	18.3 × 12.5 cm., No. 7 frame.
Average			*0.076*	*0.9*	

water content of the soap and on the water content of the surrounding air. The water content of air can be regulated experimentally in a desiccator which contains sulfuric acid of various concentrations.   For each concentration of

sulfuric acid there is a certain fixed concentration of water in the air above the liquid and it can be expressed as relative vapor pressure. The lowest vapor pressure will prevail above the most concentrated sulfuric acid.

TABLE VI-7

DATA FOR COOLING SOAP IN MACHINES[75]

Soap plate thickness, mm.	a	b
90	0.17	0.35
80	0.18	0.29
70	0.185	0.22
60	0.19	0.11

Dry powdered sodium stearate was kept over sulfuric acid at various concentrations and the water absorbed was measured after the sample had reached constant weight (Table VI-8[76]). The degree of absorption can be

TABLE VI-8

WATER ABSORPTION BY SODIUM STEARATE[76]

Rel. vapor pressure at room temp.	Absorption of water, %
0.010	0.81
0.083	2.85
0.278	2.98
0.517	3.90
0.788	10.6
0.853	13.7
0.914	20.4
0.962	38.2

expressed by stating the amount of water in grams absorbed by one gram of soap at maximum absorption.

The hydration curve in Fig. VI-7 explains that up to about 50% relative humidity the soap does not absorb appreciable quantities of water from the air, while beyond this point any small change in humidity is followed by an ever increasing degree of hydration. (Compare with hydration isotherms of McBain, Fig. IV-6.)

Water absorption or swelling of soaps will always occur whenever the air contains water vapor with a higher vapor pressure than the water contained in the soap. The volume of the soap that has undergone swelling will not be equal to the sum of the volume of the components soap and water. Rather, it will have a smaller volume. Swelled soap must consequently have a relatively higher specific gravity than soap which did not absorb water.

[76] H. Katz, *Kolloidchem. Beih.*, 9, 102 (1918).

Merklen[77] measured the water absorption of soaps by soaking cakes of Marseille soap in pure water and in water containing salt solutions of varying concentrations. He observed that while soap absorbs pure water or water from weak salt solutions it tends to give up water to concentrated salt solutions.
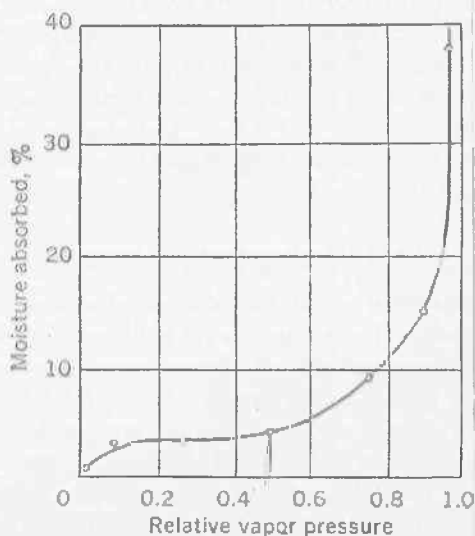
Fig. VI-7. Water absorption by sodium stearate.

The values in Table VI-9 indicate that between 15 and 20% concentration of the salt solution the water absorption of soap from salt solution becomes smaller, and in the 20 to 25% range there is a concentration at which neither absorption nor evaporation of water occurs. After this point, the soap starts to give up considerable amounts of water to the solution.

TABLE VI-9

WEIGHT INCREASE OR DECREASE OF SOAP FROM SALT SOLUTIONS OF
VARYING CONCENTRATION AFTER ELEVEN DAYS[77]

Concentration of salt solution, %	10	15	20	25
Weight increase or decrease, %	+ 3.27	+ 3.70	+ 0.98	− 5.37

(10) Heat of Hydration

Water absorption by soap is accompanied by the production of a certain amount of heat, which is called the *heat of hydration*. Lederer[18] measured the amount of heat liberated by powdered neat soaps when undergoing solution in a calorimeter.

[77] F. Merklen, *l.c.*, p. 35.
[78] E. L. Lederer, *l.c.*, p. 34.

Spontaneous combustion of soap products seem to be initiated by the heat of swelling which accompanies water absorption by dry soap. Soap powder and soap flakes have been observed to undergo spontaneous heating on many occasions, particularly in the center of a bin full of soap flakes or, even in the center of paper bags filled with soap powder.[79] It was found that only certain types of soap exhibited this phenomenon, particularly when two batches of soap flakes of different moisture content were mixed. However, experience shows that it is not possible to cause soap powder or soap flakes to undergo spontaneous combustion by mere hydration, and it is more than likely that auxiliary factors were at work, such as hydrolysis accompanied by oxidation of the fatty molecules.

(11) Drying Out of Soaps

In the same manner as soaps are able to absorb water from the air when the vapor pressure of water in the air is higher than that of the water in the soap itself, the soaps will give off water to the air if there is less water in the air. In order to know to what extent a piece of solid soap will dry out under certain conditions we will need to know the original degree of moisture absorption, the geometric form and dimensions, the time elapsed, the vapor pressure and temperature of the surrounding atmosphere, and the change in the degree of absorption at various time intervals.

The chemical composition, the method by which the soap had been manufactured, and its thermal and mechanical pretreatment will also influence to a certain degree the rate at which the soap will dry out.

A water molecule has to migrate somehow to the surface of the soap cake in order to escape into the atmosphere. Thus, a diffusion process of the water molecules from centers of a high degree of absorption to drier parts of the cake always precedes evaporation into the air proper. Of course, evaporation must take place on the surface, and a constant diffusion of water molecules from the inner parts to the surface is thus going on whenever the atmospheric conditions are favorable for evaporation. Diffusion proper within the cake is directly proportional to the difference in water concentration between two points in question.

Lederer[80] expressed this by a mathematical formula in which C is the concentration of water in the soap cake after t days; C_a is the concentration of water in the surrounding air, C_i is the concentration of water in the cake before drying, h is the half thickness of the soap slab, x is a room coordinate fixing a certain point within the slabs, and k is a constant:

$$C = C_a + (C_i - C_a) \; sin \frac{x}{h} \cdot \frac{r^2 \, k}{4 \, h^2} \cdot t$$

[79] E. J. Better, *The Industrial Chemist*, Sept., 1939.
[80] E. J. Lederer, *l.c.*, p. 42 and p. 48.

By using this equation it is possible to calculate the concentration of water at any point of the drying out process of a soap cake. The constant k was termed by Lederer the *permeation coefficient* and expresses the amount of water migrating through the unit area of a square millimeter during one day at a unit difference in concentration.

The value of the permeation coefficient depends on (*1*) the soap composition, (*2*) the method of manufacture (*3*) the method by which the soap has been solidified from the molten state, and (*4*) whether or not the soap contains electrolytes. In Table VI-10 the value of k for different soaps and at various temperatures are collected and by comparing these figures it becomes clear why certain soaps dry out at quite different rates from others.

TABLE VI-10

VALUES OF THE PERMEATION COEFFICIENT FOR SOAPS[8]

Kind of soap	Temp., °C.	k	Remarks
Milled soap	27	0.265	
Neat soap	17	0.371	
	17	0.362	
	17	0.362	
	17	0.273	From cooling press.
Cold-made soap (coconut oil)	27	0.392	KOH : NaOH = 1 : 4.
	17	0.570	
	17	0.525	
	17	0.498	KOH : NaOH = 0 : 1.
	17	0.913	KOH : NaOH = 0 : 1.
	17	0.865	KOH : NaOH = 0 : 1.
	47	1.477	KOH : NaOH = 0 : 1
Curd soap	25	0.995	Containing niger-free NaOH 1.068%.
	50	1.814	" " " "
	25	1.348	" " " "
	50	2.272	

The value of this permeation coefficient is directly proportional to the temperature. In order to study the influence of the thermal prehistory of the soap on the value of the permeation coefficient, four samples of a neat soap with 31.1% water were dried at 18°C. and at normal air humidity in order to determine the respective values of k. Sample 1 (Table VI-11) was allowed to solidify slowly in a large frame during a period of two days; sample 2 solidified in a 2-cm. layer during half a day at 25°C.; sample 3 was cooled in a cooling frame of 5-cm. plate thickness at 8°C.; and sample 4 was cooled in a 2 cm. layer at 0°C. during 15 minutes.

The influence of the fat charge on the rate of drying out can be estimated from k values for different pure soaps as calculated from results received by

Godbole and Joshi[81] in investigations of the hydration of individual soaps. These values (Table VI-12) are of relative interest only, but give an approximation of the real relation.

The water molecules migrate more slowly in a soap which possesses a low k value than in a soap with a higher value which will, consequently, tend to dry out at a quicker rate. In view of this, the values in Table VI-13 express the fact that in high molecular soaps the water is bound more strongly and is retained longer than in soaps containing low molecular fatty acids. Un-

TABLE VI-11

PERMEATION COEFFICIENTS OF SOAPS COOLED UNDER VARIOUS CONDITIONS[80]

Sample	1	2	3	4
k, mm.²/day	0.576	0.486	0.371	0.244

saturated fatty acids in their soaps dry out more quickly than saturated soaps of the same chain length. Sodium soap binds water more strongly than the corresponding potassium soaps.

Let us now consider the drying out of a cake of soap of cubical shape having a thickness of 50 mm. ($2h = 50$). The original concentration of the soap was 62% fatty acid hydrate, corresponding to about 28% of water ($C_i = 28$); humidity in air 75%; temperature 17°C. (δ); time of drying 28 days. C_a, the concentration of water in air, can be determined when the temperature and

TABLE VI-12

PERMEATION COEFFICIENTS FOR DIFFERENT SODIUM AND POTASSIUM SOAPS[81]

Soap	k	
	Sodium	Potassium
Capronate	0.295	0.305
Caprylate	0.187	0.310
Stearate	0.082	0.115
Oleate	0.117	0.190

the relative humidity are known. k for a neat soap at 17°C. is known (Table VI-10). The concentration of water in a soap cake, C_i, must be regarded initially as the same everywhere within the cake. A difference in concentration exists, only at the surface, where C_i is greater than C_a, and the soap gives up water to the air. At this point the equilibrium will be disturbed between the surface layer and the adjacent inner layer of the soap, and some migrating will start from the inner strata in the direction of the surface; from this point on the water molecules from more and more layers near the center of the cake gradually begin to migrate outward. Lederer calculated the water

[81] Godbole and Ioshi, *Allgem. Oel u. Fettzeitg.*, 27, 77 (1930).

concentration of such layers in accordance with the above data. Fig. VI-8 shows the cubical cake with the calculated boundaries representing the water concentration in each following layer in per cent of the original water concentration of the soap before starting the drying out process. These boundary lines are called *isohygrens*, because along each line, at any point, the soap has the same water and fatty acid concentration, in this case after a drying period of 28 days. In the case presented, the calculation of the isohygrens show that, after 28 days, beyond the depth of about 20% from the edges, the soap still remained in the same state as before the drying out started.

The velocity of evaporation from the surface layer is generally higher than the rate at which the water is replaced from the center of the cake. Whenever quick drying of a soap cake is attempted, the drying is localized and a hard surface layer is produced that prevents further drying of the core. Slow drying, however, yields uniformly dried soap.
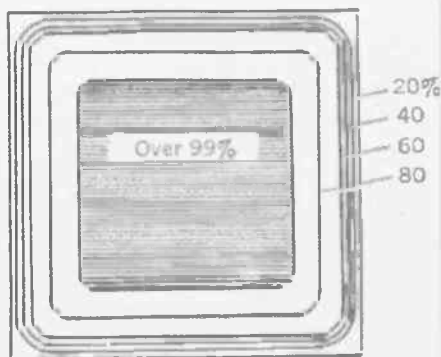
Fig. VI-8. Isohygrens of a cubical cake.[80]

When a piece of soap has reached a condition in which, as represented by Fig. VI-8, the core is still fully hydrated and the external layers are gradually dried out, diffusion of the water molecules will take place, even when, for some reason, there is no opportunity for the water at the surface to evaporate into the surrounding air. In soap cakes dried and packed into cases, layers already dried will therefore be rehydrated to a certain extent from the more hydrated inner layers. This is why finished and packed soap must never be considered as a system in equilibrium.

(12) Migration of Components in the Solid Soap

It was Kristen[82] who proved that, in a piece of solid soap, electrolytes, glycerine, and other components move by diffusion between the more hydrated

[82] W. Kristen, *Seifensieder Ztg.*, 57, 423 (1930).

core and the dried surface. The salt content of the central part is always higher than in the layers nearer the surface. Concentration in the core may be two to four times as high as in the surface layer. See Table VI-13.

In the course of these experiments it was also shown that, while the content of free caustic soda constantly increases in layers nearer the center of the cake, the content of soda ash shows tendencies of decreasing when determined on samples of the same layers.

The higher salt concentration in the center may be explained by the presence of osmotic phenomena, due to the fact that concentration differences in water between the core and surface exist. Electrolytes must migrate in the direction of higher water concentration in order to reduce the higher osmotic pressure prevailing in the region of isohygrens with low water concentration. The differences in $NaOH$ and Na_2CO_3 content seems, however, to be

TABLE VI-13

CHANGE IN PROPERTIES OF SOAPS AT DRYING[82]

Brand of soap	NaCl, %			FA content, %		
	Skin	Core	Diff., skin — core	Skin	Core	Diff., skin — core
1	0.406	0.710	0.304	82.65	80.57	2.08
2	0.250	1.050	0.800	80.43	78.84	1.57
3	0.458	0.755	0.297	82.01	79.66	2.35
4	0.311	0.877	0.566	82.59	78.77	3.82
5	0.281	0.521	0.240	81.97	78.88	3.09
6	0.306	0.957	0.651	83.58	78.92	4.66
7	0.484	0.725	0.241	82.04	81.44	0.60
8	0.322	0.542	0.220	83.58	82.55	1.03

caused not only by diffusion, but also by carbonating of the free caustic soda under the influence of the carbon-dioxide in the air. The saponification of unsaponified oil in the soap by free caustic soda may play its role in these processes as well. See Table VI-14.

(13) Sweating of Soap Cakes

Having explained the rules according to which water, glycerine, and electrolytes can migrate within the solid soap and water evaporate from the surface or even condense from the surrounding air on the surface of the soap, it is possible to explain the occurrence of *sweating*.

It was stated that water is given up to the atmosphere whenever the concentration of water in the interior of the cake and the temperature is such that the vapor pressure within is greater than that of the water in the air at that temperature. On the contrary, when the relative humidity of the air is high and such air comes into contact with the relatively dry and cool soap surface,

water is condensed there, especially when the vapor-saturated air undergoes a drop in temperature.

The condensed water forms small droplets or beads on the surface of the cake, and this new phase now behaves in relation to the soap as is expected— it tries to form an equilibrium by mutual exchange of components. Soap, electrolytes, and glycerine migrate to the surface and eventually dissolve in the droplets. Conversely, the water from the droplets tries to disappear into the dried surface layer of the soap. In this way, by the gradual diminishing of the quantity of the water droplets and by their steady enrichment in respect to electrolytes coming from inside the soap, an electrolyte concentration in

TABLE VI-14

ELECTROLYTE CONVERSION IN SOAPS AT AGING[62]

Age, days	Layer	FA content	H_2O content	Na_2CO_3 content	NaOH content	Concn. in water of	
						Na_2CO_3	NaOH
0	—	62.08	31.55	0.115	0.097	0.363	0.307
11	1	74.61	18.27	0.130	0.025	0.72	0.137
	2	67.93	25.21	0.197	0.076	0.785	0.30
	3	65.50	27.86	0.151	0.080	0.545	0.290
	4	64.89	28.50	0.129	0.080	0.455	0.280
	5	64.67	28.73	0.127	0.094	0.445	0.330
17	1	75.36	17.15	0.174	0.014	1.01	0.08
	2	69.40	23.60	0.285	0.031	1.21	0.13
	3	67.00	26.20	0.205	0.033	0.795	0.13
	4	66.48	26.67	0.160	0.079	0.60	0.30
	5	66.34	26.51	0.142	0.099	0.54	0.37
38	1	80.72	11.44	0.183	None	1.61	None
	2	77.16	15.30	0.254	0.0278	1.66	0.182
	3	74.48	18.40	0.244	0.0309	1.33	0.168
	4	71.16	21.79	0.239	0.0533	1.10	0.245

the droplets is created eventually at which the soap neither absorbs nor releases water.

The experiment of Merklen recorded in Table VI-9 shows that while soap absorbs some water from solutions of low electrolyte concentration, it gives up water to highly concentrated solutions. There is ultimately one electrolyte concentration in the solution at which the soap cake remains in equilibrium with the solution and no further exchange of water takes place beyond this stage. In the case of condensation of water on the soap surface, the electrolyte concentration increases at a rate at which (a) the water penetrates into the soap and (b) the electrolytes reach the surface.

It is obvious that the equilibrium electrolyte concentration may be reached with various quantities of water present at the surface. For instance, with a high rate of migration of electrolytes, the water droplets may reach the

required concentration when relatively large quantities are still present at the surface. In this case, there are always large quantities of beads of sweat on the soap and the soap tends to become wet. This probably happens because the soap contains large quantities of electrolytes. On the other hand, when conditions cause a high rate of water diffusion from the surface into the soap, together with slow electrolyte migration, the soap, of course, assumes a dry appearance.

White precipitates are known to form on the soap surface under certain conditions. This happens when for some reason the saturation concentration of the solution in respect to salts at the surface has been exceeded.

PART B

RAW MATERIALS OF SOAP MANUFACTURE

Inorganic and Organic Soap Builders and Fillers, etc.

WATER

Water is an important raw material in the manufacture of soap. Whether it is hard or soft has little material effect on normal soapboiling because any hardness present is converted into lime soaps, which go into the product. However, this represents a loss. For example, under normal boiling conditions, when 100 lbs. of lye is produced for every 100 lbs. of fat saponified, the presence of 200 p.p.m. of hardness, expressed as $CaCO_3$, would be approximately 0.08% soap lost through softening. Since soapboiling losses through other factors may be as high as 1%, this is not too significant. However, when soluble soaps such as liquid potash soaps are made, slight water hardness causes great difficulty in obtaining clear solutions and the water must be softened. In addition to this the boiler department of each plant must have its water treated for hardness—as in any other industrial plant. But even aside from these considerations it is important that the student of soap manufacture know something of water hardness and its softening, if for no other reason than to gain some insight into one of the chief drawbacks of soap as a detergent agent and the processes available for rectification.

Before dealing with the softening process, something must be said about the substances which render a natural water hard, and how this "hardness" is defined.

Hardness is often expressed in degrees or grains per United States gallon. One degree of hardness indicates the presence of calcium and magnesium and other soap-precipitating compounds in an amount equivalent to 1 grain of calcium carbonate per United States gallon. Hardness is now more often expressed in parts per million of water.

Some conversion factors are:

Grains per U. S. gallon $\times$ 17.15 = p.p.m.
Grains per Imperial gallon $\times$ 14.29 = p.p.m.
p.p.m. $\times$ 0.0583 = grains per U. S. gallon.
p.p.m. $\times$ 0.07 = grains per Imperial gallon.
lbs. per million/120 = lbs. per 1000 U. S. gallon.
lbs. per million/100 = lbs. per 1000 Imperial gallon.

Water with up to 100 p.p.m. hardness is usually considered as "soft"; up to 200 p.p.m. it is considered as "moderately hard"; 200–300 p.p.m. indicate very hard water.

Hardness is of two kinds: (a) *Temporary hardness* caused by calcium and magnesium bicarbonates, which could be removed simply by boiling the water, thus transforming the soluble bicarbonates into the practically insoluble carbonates with the evolution of carbon dioxide. As temporary hardness is usually present together with permanent hardness, both are removed with a single treatment. (b) *Permanent hardness* is caused by all other soluble salts of calcium and magnesium, *e.g.*, chlorides and sulfates. This hardness can be removed only by chemical treatment or distillation.

Two principal methods of chemical treatment of water are to be distinguished. The *internal* treatment consists of treating the boiler feed water with chemicals before it enters the boiler. Hardness is precipitated *within* the boiler as sludge and not as scale. This process is less common than the external process, especially in the soap industry, where it is never used. The *external* process consists in removing the main part of hardness outside the boiler. For the soap industry it may often be practical to treat the water added during the soapboiling process in the same way as the boiler feed water.

Two methods are comonly used:

(1) The Lime–Soda Process

This method is usually employed for softening waters of medium and high hardness. It is a process in which the scale-forming salts are precipitated by the use of lime and soda ash or, in certain cases, caustic soda. The process is much more efficient in the hot than in the cold and the hot process should be employed wherever possible.

The typical equations for this process are:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow MgCO_3 + CaCO_3 \downarrow + H_2O$$

In the latter case, since $MgCO_3$ is fairly soluble, it is further transformed into $Mg(OH)_2$ according to the following equation:

$$MgCO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaCO_3 \downarrow$$
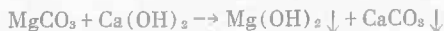
For soluble salts of Ca or Mg the following equations are typical (here Na_2CO_3 comes into the picture):

$$MgCl_2 \text{ (or } MgSO_4) + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaCl_2 \text{ (or } CaSO_4)$$

$$CaCl_2 \text{ (or } CaSO_4) + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaCl \text{ (or } Na_2SO_4)$$

$$MgSO_4 \text{ (or } MgCl_2) + Ca(OH)_2 + Na_2CO_3 \rightarrow Mg(OH)_2 \downarrow + CaCO_3 \downarrow + Na_2SO_4 \text{ (or } 2NaCl)$$

When water contains appreciable quantities of magnesium salts and has been treated by the lime–soda process, precipitation may continue for a considerable period. The use of some modern types of lime–soda plants in which the reaction takes place in the presence of agitated sludge or sand results in a reduced retention time in the softener and decreased after precipitation.

The efficiency of the lime–soda process can be improved by adding about 3 p.p.m. dry sodium aluminate calculated on water added to the lime–soda slurry. This will facilitate precipitation and permit working at such low temperatures as 45°C.

(2) The Ion Exchange Process

This method may be used to remove practically all hardness. It is often employed combined with a pretreatment with lime–soda if very hard water is to be dealt with. The scale-forming salts are converted to the equivalent non-scale-forming sodium salts by the passage of the water through a bed of base-exchanging material such as Zeolites. The standard plant for the application of the process usually comprises a cylindrical unit containing the bed of Zeolite material together with equipment for preparing and storing the salt solution used for the regeneration of the Zeolite.

Zeolites or Permutits are either natural or synthetic base exchange silicates of the following general formula:

$$Na_2O \cdot R_2O_3 \cdot xSiO_2 + 10H_2O$$

where R_2O_3 stands for an amphoteric metal oxide, usually Al_2O_3 or Fe_2O_3. Zeolites are water insoluble, but their base (Na) is interchangeable with the bases of soluble salts as Mg and Ca. The reactions occurring are typified by the following equations. The complex Zeolite radical is represented by the symbol [Ex].

$$CaHCO_3 + Na_2[Ex] = Ca[Ex] + 2NaHCO_3$$

$$CaSO_4 + Na_2[Ex] = Ca[Ex] + Na_2SO_4$$

$$MgCl_2 + Na_2[Ex] = Mg[Ex] + 2NaCl$$

$$MgSO_4 + Na_2[Ex] = Mg[Ex] + Na_2SO_4$$
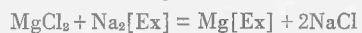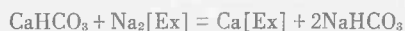
After the Zeolites are exhausted, they may be regenerated by treatment with a 5–10% brine solution. The reaction occurs according to the following equation:

$$Ca[Ex] \text{ or } Mg[Ex] + 2NaCl = Na_2[Ex] + CaCl_2 \text{ or } MgCl_2$$
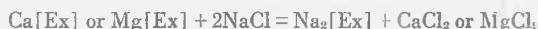
In practice the Zeolites are regenerated when the desired degree of hardness is no longer obtained. It will be noted that for the hardness-forming earth alkaline salts soluble alkali salts are left in solution.

Since the Zeolites also exert a filtering action, regeneration with brine is usually combined with an efficient "backwash" to remove every sediment from the Zeolite bed and to regrade it hydraulically.

Newly developed synthetic resin ion exchangers have made possible deionizing water completely by successive treatment with cation and anion exchangers.[1] Water is passed through a first ion exchanger. When water containing calcium, magnesium, sodium, and other metal ions is passed through it, they are converted into their equivalent amounts of acids, *i.e.*, the the calcium and magnesium carbonate are converted to carbon dioxide, calcium and magnesium sulfates are changed to sulfuric acid, sodium or calcium chlorides are changed to hydrochloric acid. In other words, all the alkaline bases in the water are removed and their salts are converted to their corresponding acids, and the water issuing from this first plant is acid, whereas it was previously alkaline.

The water from this first unit is then passed through a second pressure cylinder. This is a plant similar to the first, but filled with a bed of acid absorption material. During its passage through this bed the whole of the acids contained in the water, other than CO_2, is absorbed by the material, leaving the water completely free of any of the minerals contained in the raw water, but still containing free CO_2.

It is worthy of note that the second is an absorption plant, as distinct from the first, which is an exchanging plant. In other words, in the first plant the alkaline salts are changed into acids, and in the second the acids are absorbed.

The final stage of the process consists in passing the water through a cold degasifier for the removal of the free CO_2.

The actual operation of this process is as simple as the salt regeneration previously mentioned. Instead of being regenerated with a salt solution, the first unit is regenerated with a very weak solution of sulfuric acid, and the second unit with a solution of soda ash.

A process for deionizing water using synthetic resins, (the Amberlites of Resinous Products & Chemical Co.) is especially suitable for small-scale operations.[2] The principal equations are:

Cation Exchange Resin

Sodium Cycle: $2NaR + CaSO_4 \rightleftharpoons CaR_2 + Na_2SO_4$
$2NaR + MgCl_2 \rightleftharpoons 2NaCl + MgR_2$
$2NaR + Ca(HCO_3)_2 \rightleftharpoons CaR_2 + 2NaHCO_3$

Hydrogen Cycle: $2HR + CaSO_4 \rightleftharpoons CaR_2 + H_2SO_4$

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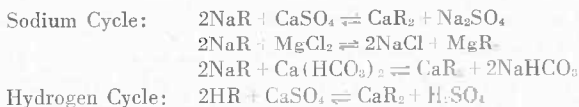
[1] *Distilled Water without Distillation*, Permutit Co.

[2] *The Amberlites, Synthetic Ion Exchange Resins*, Resinous Products & Chemical Co., Philadelphia, Pa.

$$2HR + MgCl_2 \rightleftharpoons MgR_2 + 2HCl$$
$$2HR + Ca(HCO_3)_2 \rightleftharpoons CaR_2 + H_2O + CO_3 \uparrow$$
$$HR + NaCl \rightleftharpoons NaR + HCl$$

NaR = sodium salt of cation exchange resin
HR = hydrogen derivative of cation exchanger

Anion Exchange Resin

Acid Removal: $2RX + H_2SO_4 \rightarrow (RX)_2 \cdot H_2SO_4$
$$RX + HCl \rightarrow RX \cdot HCl$$

RX = anion exchange resin with the acid-binding substituent X
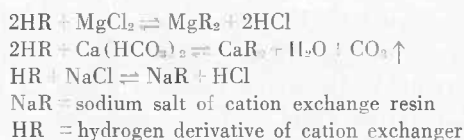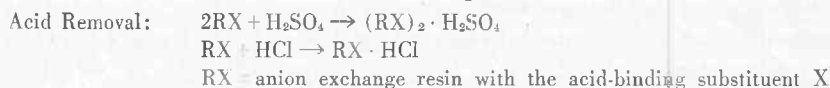
Regeneration of the cation exchangers is possible, as can be seen from the above equations. The reaction of the cation exchangers, a true equilibrium reaction, is governed by the law of mass action, and an increase in the concentration of the products effects a reversal of the equilibrium. Generally, an appreciable excess of the regenerant is used, and a relatively high concentration is employed so that regeneration of the exchanger is essentially complete. However, as might be anticipated. complete regeneration is not economical. so that an optimum regeneration value is chosen.
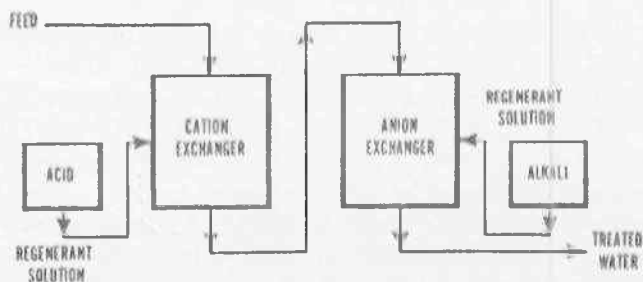
Fig. VII-1. Deionization of water—flow sheet.[3]

Although the mechanism of reaction of the acid absorbent is thought to be different, regeneration can likewise be effected. Treatment of the depleted anion exchanger with sodium carbonate solution neutralizes the acid which has been fixed, and frees the anion exchanger for further acid adsorption. For example:

$$RX \cdot HCl + Na_2CO_3 \rightarrow RX + NaCl + H_2O + CO_2$$

(depleted   (regenerated
anion   anion
exchanger)   exchanger)
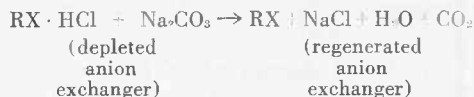
The flowsheet for complete deionization gives a clear picture of the process (see Fig. VII-1[3]).

(3) Phosphates for Water Treatment

Monosodium, disodium, and trisodium phosphates are frequently used to form an easily removable soft phosphate sludge. The more modern sodium

[3] Eric Kunnas, Jr., *Drug & Cosmetic Industry*, July, 1945, p. 49.

hexametaphosphate $(NaPO_3)_6$ (sometimes simply called metaphosphate) forms soluble complexes with the alkaline earth ions or with residual iron or alumina ions. Its valuable dispersing property makes it a very important soap builder and laundering agent. (The phosphates will be discussed in detail in Chapter IX-5.) The dispersing properties of metaphosphates led to the development of the so-called *threshold treatment* after the softening process with lime–soda. Small additions of 5 p.p.m. and even less of $(NaPO_3)_6$ prevents the after precipitaton of calcium carbonate. The use of metaphosphate (Calgon) for complete softening is not very frequent. For every 10 p.p.m. hardness 0.7 part metaphosphate would have to be added to 100,000 parts water. Another phosphate of the modern type is sodium tetraphosphate (Quadrafos, Rumford Chemical Works) $(Na_6P_4O_{13})$, which is also used for aftersoftening treatment of water, where it is more effective than metaphosphate in dispersing magnesium salts, but less effective in dispersing calcium salts.

(4) Oxygen Removal

It must be mentioned that other factors besides hardness are to be considered as well, *e.g.*, dissolved oxygen may be a serious troublemaker especially for the modern high pressure steam generators, where it causes severe corrosion. Water ordinarily saturated with air at 10°C. (50°F.) contains about 8 cc. oxygen per 1000 cc. water. This may be removed by spraying or by cascading the water down over a series of trays contained in a tank. During the downward flow the water is scrubbed by rising steam. An open feed water heater of the spray type will usually lower the dissolved oxygen content to below 0.3 cc. per liter. Scrubbing devices will remove even this small amount, or it can be chemically combined using a scavenger like sodium sulfite:[4]

$$O_2 + 2Na_2SO_3 \rightarrow 2Na_2SO_4$$

As this complete or nearly complete removal of oxygen is necessary only for boiler feed water, the water used during the soap boiling process will not go through this procedure.

(5) Removal of Iron

The removal of iron from water for the soap boiling process is of specific importance, as iron left in the soap may cause serious deterioration and lower the keeping characteristics of the ready made soap. But fortunately iron is usually removed to a sufficient degree by most municipal water stations; otherwise, treatment with small amounts of metaphosphate or tetraphosphate has great advantage.

[4] R. N. Shreve, *The Chemical Process Industries*, McGraw-Hill, New York, 1945, p. 57.

THE CAUSTIC ALKALIES

(1) Caustic Soda

Caustic soda (NaOH)[5] ranks first among the alkaline soap builders, since only caustic soda (or caustic potash) is able to saponify the neutral fat or oil which constitutes the main fat stock used in soapmaking under ordinary soap-boiling conditions. United States soap factories consume 5–6% of the caustic soda produced in the country.

By far the greatest part of caustic soda is produced by electrolysis, according to the equation:

$$2NaCl \rightarrow 2NaOH + H_2 + Cl_2$$

When electrolysis is carried out in the *diaphragm cell*, the salt brine first passes into the anode compartment where part of the chlorine is released, and then through the porous diaphragm (usually made of asbestos fibers) into the cathode compartment where the sodium hydroxide is formed. The brine flowing into the cathode compartment contains dissolved chlorine which reacts with the hot caustic solution to form sodium chlorate. This weak liquor is concentrated to a 50% NaOH concentration and the excess salt, which precipitates, is removed.

The *mercury cell* for electrolysis is more expensive to operate because of the high investment in mercury; and because of the higher voltage required for operation a higher power cost results. In this cell, mercury forms the cathode, and metallic sodium released by the passage of the current amalgamates with the mercury. Reaction of the amalgam with water produces a caustic soda solution of exceptional purity.

[5] Material for this chapter on caustic soda was kindly supplied by Michigan Alkali Company, Wyandotte, Michigan.

The nonelectrolytic lime–soda process is still used to some extent. In this process a soda ash solution is causticized by the addition of lime according to the equation:

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3$$

Since calcium carbonate is less soluble than calcium hydroxide, the equilibrium is shifted to the right so that about 90% of the sodium carbonate is converted to sodium hydroxide. The precipitated calcium carbonate and the excess calcium hydroxide are removed by settling and filtration, resulting in a clear liquor containing about 12% NaOH and 1.7% Na_2CO_3. This weak liquor is concentrated in multiple-effect evaporators to a 50% NaOH content. In an increasing concentration of NaOH, the Na_2CO_3 becomes less soluble and is finally precipitated; the final 50% solution contains only 0.15% Na_2CO_3. For anhydrous caustic the water is driven off by heating in large cast-iron pots of 14- to 20-ton capacity. The molten anhydrous caustic may be either cast into drums or flaked on a water-cooled rotary drum.

It is important for the modern soap technician to be well acquainted with the physical and chemical properties of the caustic raw material of soap manufacture.

Caustic soda or sodium hydroxide is a compound having the chemical formula NaOH and a molecular weight of 40.01. When crystallized from solution, the anhydrous material and all the hydrates are colorless; the commonly known product solidified from the molten state has a crystalline fracture and appears white. It has a specific gravity of 2.13 and melts sharply at $318°C.$, with a latent heat of fusion of 40 cal. per gram. Two anhydrous crystalline modifications exist, the transition occurring at $300°C.$, with the liberation of heat of transition of 25 cal. per gram.

NaOH is highly hygroscopic. The usual grade of purity of high-grade commercial NaOH in the United States is approximately 76% $Na_2O = 98\%$ NaOH. A.S.T.M. Designation D456-39 gives the following requirements as to chemical composition:

Total alkalinity as Na_2O	75.5% (min.)
Sodium hydroxide (NaOH)	96% (min.)
Carbonate as Na_2CO_3	2% (max.)

Undiluted caustic soda should be purchased by net weight and is usually sold solid, ground, powdered, or flaked, in drums. Caustic soda solutions of specified concentrations are usually delivered to the consumer in tank cars.

Solid caustic soda, when exposed to the air, absorbs water and carbon dioxide to form sodium carbonate, Na_2CO_3.

Table VIII-1 gives the relation of specific gravity to percentage NaOH. The change in specific gravity with temperature is given in Table VIII-2.

[6] Based on tables from *International Critical Tables.*

TABLE VIII-1

Baumé Concentration Table for Caustic Soda Solutions at 15.6°C. (60°F.) [6]
Based on Tables from International Critical Tables

Baumé Am. Std.	NaOH. %	Sp./gr. 60/60°F.	Twaddell	Na₂O, %	NaOH, g./l.	NaOH, lbs./gal.	NaOH, lbs./cu.ft.	Total wt. soln., lbs./gal.	Total wt. soln., lbs./cu.ft.
1	0.603	1.007	1.4	0.47	6.06	0.05	0.38	8.39	62.80
2	1.22	1.014	2.8	0.95	12.35	0.10	0.77	8.45	63.24
3	1.85	1.021	4.2	1.43	18.87	0.16	1.18	8.51	63.69
4	2.49	1.028	5.6	1.93	25.61	0.21	1.60	8.57	64.14
5	3.15	1.036	7.1	2.44	32.57	0.27	2.03	8.63	64.60
6	3.81	1.043	8.6	2.96	39.75	0.33	2.48	8.69	65.06
7	4.49	1.051	10.1	3.48	47.15	0.39	2.94	8.76	65.53
8	5.18	1.058	11.7	4.02	54.79	0.46	3.42	8.82	66.01
9	5.88	1.066	13.2	4.56	62.65	0.52	3.91	8.88	66.50
10	6.59	1.074	14.8	5.11	70.73	0.59	4.42	8.95	66.99
11	7.31	1.082	16.4	5.67	79.06	0.66	4.94	9.02	67.49
12	8.05	1.090	18.0	6.24	87.65	0.73	5.47	9.09	68.00
13	8.79	1.098	19.7	6.81	96.47	0.81	6.02	9.15	68.51
14	9.55	1.107	21.4	7.40	105.5	0.88	6.59	9.22	69.04
15	10.31	1.115	23.1	7.99	114.9	0.96	7.17	9.29	69.57
16	11.09	1.124	24.8	8.59	124.5	1.04	7.78	9.37	70.11
17	11.88	1.133	26.6	9.21	134.4	1.12	8.40	9.44	70.65
18	12.69	1.142	28.3	9.83	144.7	1.21	9.03	9.51	71.21
19	13.50	1.151	30.2	10.46	155.2	1.30	9.69	9.59	71.77
20	14.33	1.160	32.0	11.11	166.1	1.39	10.37	9.67	72.35
21	15.18	1.169	33.9	11.76	177.3	1.48	11.07	9.75	72.93
22	16.04	1.179	35.8	12.43	188.8	1.58	11.79	9.82	73.53
23	16.91	1.189	37.7	13.10	200.7	1.68	12.53	9.90	74.13
24	17.79	1.198	39.7	13.79	213.0	1.78	13.30	9.99	74.74
25	18.70	1.208	41.7	14.49	225.6	1.88	14.09	10.07	75.36

TABLE VIII-1 (*continued*)

Baumé Am. Std.	NaOH, %	Sp./gr. 60/60°F.	Twaddell	Na₂O, %	NaOH, g./l.	NaOH, lbs./gal.	NaOH, lbs./cu.ft.	Total wt. soln., lbs./gal.	Total wt. soln., lbs./cu.ft.
26	19.62	1.218	43.7	15.20	238.8	1.99	14.91	10.16	76.00
27	20.55	1.229	45.8	15.92	252.3	2.11	15.75	10.25	76.64
28	21.51	1.239	47.9	16.66	266.2	2.22	16.62	10.33	77.30
29	22.48	1.250	50.0	17.42	280.6	2.34	17.52	10.42	77.96
30	23.47	1.261	52.2	18.18	295.6	2.47	18.45	10.51	78.64
31	24.47	1.272	54.4	18.96	310.9	2.60	19.41	10.60	79.33
32	25.50	1.283	56.6	19.76	326.9	2.73	20.41	10.70	80.03
33	26.54	1.295	58.9	20.56	343.2	2.86	21.43	10.79	80.74
34	27.62	1.306	61.3	21.40	360.4	3.01	22.50	10.89	81.47
35	28.72	1.318	63.6	22.25	378.2	3.16	23.61	10.99	82.22
36	29.85	1.330	66.1	23.13	395.7	3.30	24.77	11.09	82.97
37	31.01	1.343	68.5	24.03	415.9	3.47	25.97	11.19	83.74
38	32.20	1.355	71.0	24.95	435.9	3.64	27.21	11.30	84.52
39	33.44	1.368	73.6	25.91	456.9	3.81	28.53	11.40	85.32
40	34.71	1.381	76.2	26.89	478.8	4.00	29.89	11.51	86.13
41	36.00	1.394	78.8	27.89	501.4	4.18	31.30	11.62	86.96
42	37.34	1.408	81.6	28.93	525.1	4.38	32.78	11.74	87.80
43	38.71	1.422	84.3	29.99	549.7	4.59	34.32	11.85	88.67
44	40.12	1.436	87.1	31.09	575.4	4.80	35.92	11.97	89.54
45	41.60	1.450	90.0	32.23	602.5	5.03	37.63	12.09	90.44
46	43.13	1.465	92.9	33.41	631.0	5.27	39.40	12.21	91.35
47	44.69	1.480	95.9	34.63	660.5	5.51	41.24	12.34	92.28
48	46.28	1.495	99.0	35.86	691.1	5.77	43.15	12.46	93.23
49	47.91	1.510	102.1	37.12	722.9	6.03	45.13	12.59	94.20
50	49.60	1.526	105.3	38.43	756.2	6.31	47.21	12.73	95.20
51	51.33	1.543	108.5	39.77	791.0	6.60	49.39	12.86	96.21

TABLE VIII-2

Specific Gravity of Caustic Soda Solutions at Various Temperatures[6]

NaOH, %	32°F. (0°C.)	50°F. (10.0°C.)	60°F. (15.6°C.)	70°F. (21.1°C.)	80°F. (26.7°C.)	100°F. (37.8°C.)	120°F.) (48.9°C.)	140°F. (60.0°C.)	160°F. (71.1°F.)	180°F. (82.2°C.)	200°F. (93.3°C.)	212°F. (100°C.)
1	1.013	1.013	1.012	1.010	1.009	1.005	1.001	0.995	0.989	0.982	0.975	0.970
2	1.025	1.024	1.023	1.021	1.020	1.016	1.011	1.006	0.999	0.993	0.985	0.981
3	1.037	1.036	1.034	1.035	1.032	1.027	1.022	1.016	1.010	1.003	0.996	0.991
4	1.049	1.047	1.045	1.043	1.042	1.037	1.032	1.026	1.020	1.014	1.006	1.002
5	1.061	1.058	1.056	1.054	1.052	1.048	1.043	1.037	1.031	1.024	1.017	1.013
6	1.072	1.069	1.067	1.065	1.063	1.058	1.053	1.047	1.041	1.034	1.027	1.023
7	1.084	1.081	1.079	1.076	1.074	1.069	1.064	1.058	1.052	1.045	1.038	1.034
8	1.095	1.092	1.090	1.087	1.085	1.080	1.075	1.069	1.062	1.056	1.049	1.044
9	1.107	1.103	1.101	1.099	1.096	1.091	1.085	1.079	1.073	1.066	1.059	1.055
10	1.118	1.114	1.112	1.110	1.107	1.102	1.096	1.090	1.083	1.077	1.070	1.065
12	1.141	1.137	1.134	1.132	1.129	1.123	1.117	1.111	1.105	1.098	1.091	1.087
14	1.164	1.159	1.156	1.154	1.151	1.145	1.139	1.133	1.126	1.119	1.112	1.108
16	1.186	1.181	1.178	1.176	1.173	1.167	1.161	1.154	1.148	1.141	1.133	1.129
18	1.209	1.204	1.201	1.198	1.195	1.189	1.182	1.176	1.169	1.162	1.155	1.150
20	1.231	1.226	1.223	1.220	1.217	1.209	1.204	1.197	1.190	1.183	1.176	1.171
22	1.253	1.248	1.245	1.242	1.239	1.232	1.226	1.219	1.212	1.204	1.197	1.192
24	1.275	1.270	1.267	1.264	1.260	1.254	1.247	1.240	1.233	1.226	1.218	1.214
26	1.298	1.292	1.289	1.285	1.282	1.275	1.269	1.262	1.254	1.247	1.239	1.235
28	1.320	1.314	1.310	1.307	1.304	1.297	1.290	1.283	1.275	1.268	1.260	1.256
30	1.341	1.335	1.332	1.329	1.325	1.318	1.311	1.304	1.296	1.289	1.281	1.277
32	1.363	1.357	1.353	1.350	1.346	1.339	1.332	1.325	1.317	1.310	1.302	1.297
34	1.384	1.377	1.374	1.370	1.365	1.359	1.352	1.345	1.338	1.330	1.322	1.317
36	1.404	1.398	1.394	1.391	1.387	1.380	1.372	1.365	1.357	1.350	1.342	1.337
38	1.425	1.418	1.415	1.411	1.407	1.400	1.392	1.385	1.377	1.369	1.362	1.357
40	1.445	1.438	1.434	1.431	1.427	1.419	1.412	1.404	1.396	1.389	1.381	1.376
42	1.465	1.458	1.454	1.450	1.446	1.439	1.431	1.423	1.415	1.408	1.400	1.395
44	1.484	1.477	1.473	1.469	1.458	1.450	1.450	1.442	1.434	1.426	1.419	1.414
46	1.503	1.496	1.492	1.488	1.484	1.476	1.469	1.461	1.453	1.445	1.438	1.433
48	1.523	1.515	1.511	1.507	1.503	1.495	1.487	1.480	1.472	1.464	1.456	1.452
50	1.542	1.534	1.530	1.526	1.522	1.514	1.506	1.498	1.490	1.483	1.475	1.470

The handling of caustic soda requires special precautions, because it is strongly corrosive to the human skin. During all operations with caustic soda workmen should wear thick cotton clothing, their hands should be protected by gloves, and they should wear safety goggles. If solid caustic soda is to be diluted, the drum metal must be removed from the solid cake. The easiest way is to place the drum on its side with the body seam up. A crowbar is inserted through the seam under the metal. The drum is then rolled back and forth with the crowbar; this will detach the body sheet from both the caustic and the ends, and the cylinder of caustic soda can then be rolled out. For preparation of solution from the solid, the cake is placed in the caustic dissolving tank by the use of a chain hoist. Workers should be instructed in safety precautions. They should wear goggles, face shields, and rubber gloves.

Practical equipment for dissolving the caustic is described by Michigan Alkali Company. (Fig. VIII-1.) In this equipment the difference in density between high and low concentrations of solution is utilized to speed up the circulation and, therefore, the rate of solution. As solution proceeds, the volume of liquor shrinks and water is added to keep the system operating.

It is possible to work with less equipment by breaking the caustic cake, and putting it in a basket or on grids under the surface of the water in a steel tank. Since the dense solution formed flows to the bottom, circulation is set up which brings a less concentrated solution to the solid.

If flakes or crystals are to be dissolved, solution proceeds so fast that little agitation is required to bring about complete dissolution in a very short time. In this case, evolution of heat may be so great that no large single quantity of flakes or crystals should be added to water above 60°C. (140°F.), as the heat of solution may bring about sudden steam evolution, with consequent danger to personnel.

Caustic soda solutions attack zinc, tin, aluminum, and brass very readily, but the effect on iron and steel (cast iron is more resistant than steel) at room temperature is very small. At elevated temperatures the attack on iron and steel becomes greatly accelerated and it becomes necessary to dissolve it at lower temperatures, or at least to cool the solutions. For this reason a cooling coil in the dissolving tank is very often an investment which pays in the long run, especially if one keeps in mind that the rate of corrosion on mild steel of 50% liquid NaOH becomes about 80 times as fast at 104°C. as at 21°C. The cracking phenomenon of corrosion on steel is called "caustic embrittlement." Places of stress are especially prone to caustic embrittlement.[6a]

Storage tanks may be constructed from welded steel plates. For riveted,

[6a] M. G. Fontana, *Ind. Eng. Chem.*, *44*, 81A, 82A, 84A (1952); H. W. Schmidt, P. T. Gegner, G. Heinemann, C. P. Poyacar, and E. H. Wyche, *Corrosion*, *7*, 295–302 (1951).
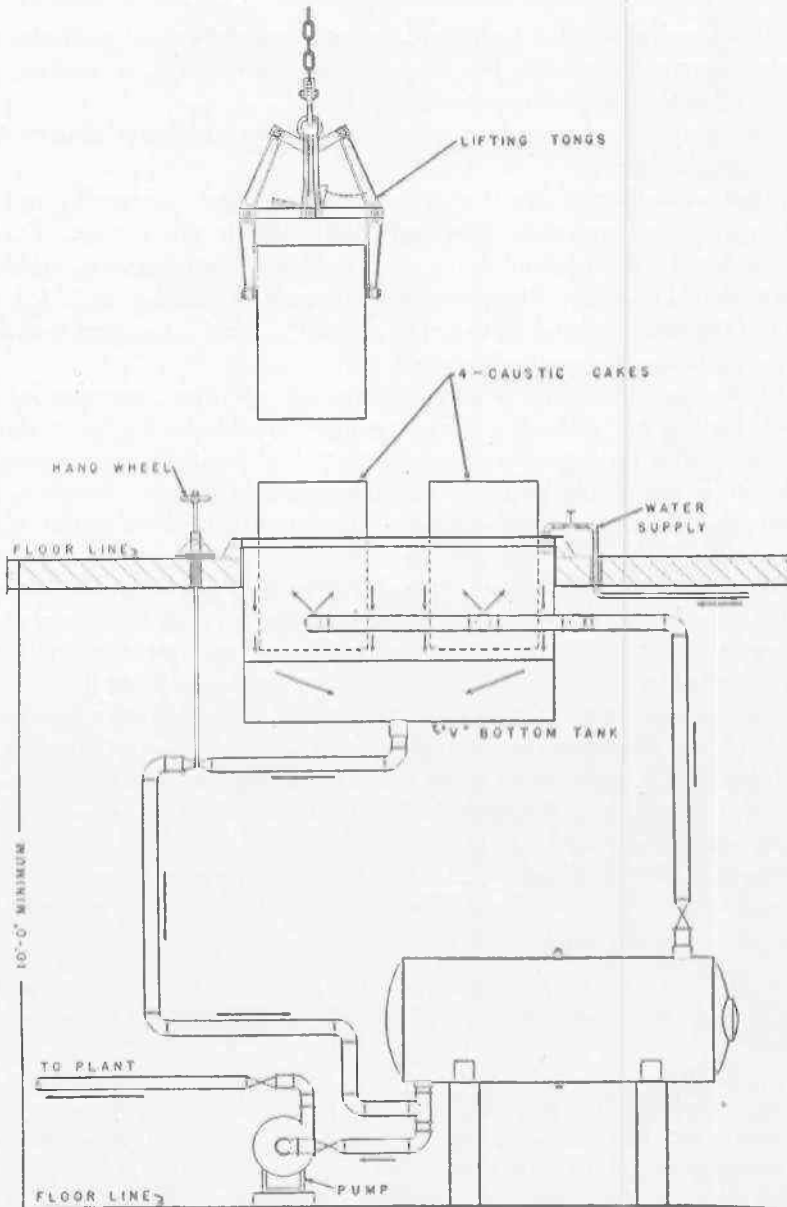
Fig. VIII-1. Dissolving unit for caustic soda or potash.[5]

vertical storage tanks containing upward of 10,000 gallons, tank steel of not less than $\frac{3}{8}$ inch should be used. Tanks in the open or subjected to temperatures lower than the freezing point of the caustic should be insulated and provided with steam heating coils.

Nickel and nickel-clad steel resist "caustic embrittlement" perfectly, and special lining paints and the like are on the market which have excellent protective value for steel and iron as well.

For pipelines, valves, and pumps, the following materials of constructions are recommended:

Standard black iron pipe is satisfactory for pipelines. Flanged joints are preferred to couplings, since couplings tend to leak in this service. Rubber is a good gasket material unless the caustic is hot, when asbestos composition gaskets should be used. Pipelines exposed to temperatures below the freezing point of the caustic should be bound to a steam line and a common insulation should be wrapped about both pipes.

All-iron cocks, preferably of the lubricated type, are recommended for caustic service, but nickel-iron cocks are more durable for high-temperature service. Valves for caustic service, if used, should be of all-iron or trimmed with Monel, nickel or any alloys recommended by the valve manufacturing firms. Brass or bronze valves or fittings must not be used for caustic under any circumstances.

All-iron centrifugal pumps with extra-deep stuffing glands are standard for pumping liquid caustic. For high-temperature use, nickel or Monel shafts give better service. The highest grade graphite asbestos packing specifically recommended for caustic soda service by the maker should be used.

It should be borne in mind that the prevention of corrosion by caustic solution is important not only from the point of view of preservation of equipment, but also from the point of view of the keeping quality of soap. As it will be explained later (Chapter XXXI, 4), traces of metal in soap have a deteriorating effect on the ready made soap.

Figure VIII-2[7] facilitates diluting or strengthening caustic soda solutions of given strength to the concentration required. The following examples are given for use of the dilution chart.[7]

A shipment of 146,000 lbs. of 74% NaOH is to be diluted with water to prepare 50% solution. How many gallons of water must be used? What will be the resulting volume?

Lay a straight edge from 74% NaOH on the strong caustic axis to 0% (water) on the diluting caustic axis. This crosses the 50% NaOH coordinate at point "a," corresponding to 67.6 lbs. of strong caustic required for every 32.4 lbs. of water (read from the top and bottom of the chart, respectively). Each pound of 74% caustic, therefore, requires 32.4/67.6, or 0.48 lbs. water. 146,000 lbs. will require 70,080 lbs. or 8,403 gal. of water (8.34 lbs. water equals 1 gal.). The volume of the 50% liquor will not be the sum of the volumes of the 74% NaOH and the water due to contraction. The weight of the 50% liquor will be 146,000 + 70,080, or 216,080 lbs. One gallon of 50% caustic liquid weighs 12.76 lbs. This figure divided into 216,080 gives 16,934 gals. as the volume of the 50% liquor.

[7] Courtesy of Michigan Alkali Company, Wyandotte, Michigan.

% NAOH IN WEAK LIQUOR TO BE STRENGTHENED
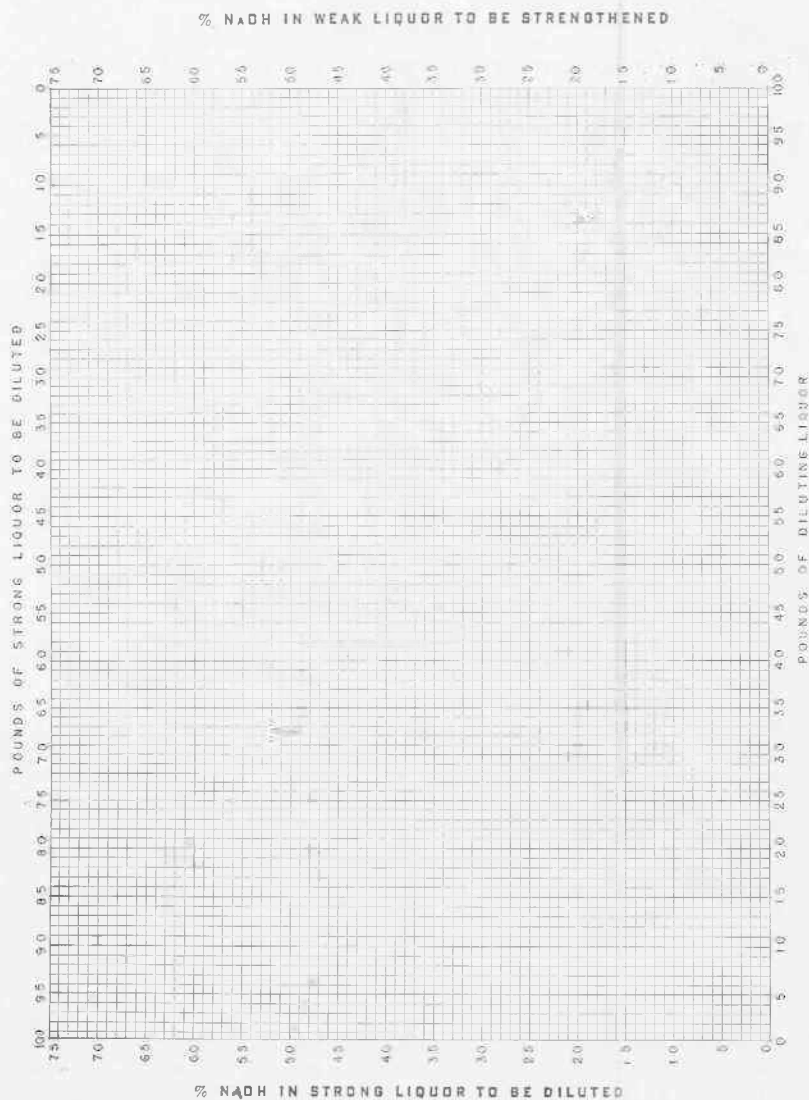
Fig. VIII-2. Chart for diluting or strengthening caustic soda solutions.[5]

1,000 gallons of 13% NaOH liquor is at hand and is to be strengthened to 18% by the addition of 50% liquor. How many gallons of 50% liquor must be added?

Connect 50% on the strong caustic axis with 13% on the diluting caustic axis. This crosses the 18% line at point "b,", corresponding to 86.5 lbs. diluting liquor and 13.5 lbs. strong liquor, or 0.156 lb. 50% liquor for each pound of 13% liquor. 1,000 gal. of 13% liquor weigh 9,548 lbs. and the total requirement of 50% liquor will be 1,489 lbs. Dividing this by 12.76 (weight of one gallon of 50% liquor at 60°F.) gives 116.7 gal. as the volume of 50% liquor to add.

TABLE VIII-3

POTASSIUM HYDROXIDE—DENSITY OF AQUEOUS SOLUTIONS AT 15°C. (59°F.)[8]

KOH, %	Sp. gr.	°Baumé	°Twaddell	KOH wt. in soln.		
				g./l.	lbs./gal.	lbs./cu.ft.
1	1.0083	1.2	1.66	10.08	0.08415	0.6295
2	1.0175	2.5	3.50	20.35	0.1698	1.270
3	1.0267	3.8	5.34	30.80	0.2570	1.923
4	1.0359	5.0	7.78	41.44	0.3458	2.567
5	1.0452	6.3	9.04	52.26	0.4361	3.263
6	1.0544	7.5	10.88	63.26	0.5280	3.950
7	1.0637	8.7	12.74	74.46	0.6214	4.648
8	1.0730	9.9	14.60	85.84	0.7164	5.359
9	1.0824	11.0	16.48	97.42	0.8130	6.082
10	1.0918	12.2	18.36	109.2	0.9112	6.816
11	1.1013	13.3	20.26	121.1	1.011	7.563
12	1.1108	14.5	22.16	133.3	1.112	8.322
13	1.1203	15.6	24.6	145.6	1.215	9.092
14	1.1299	16.7	25.98	158.2	1.320	9.874
15	1.1396	17.8	27.92	170.9	1.427	10.67
16	1.1493	18.8	29.86	183.9	1.535	11.48
17	1.1590	19.9	31.80	197.0	1.644	12.30
18	1.1688	20.9	33.76	210.4	1.756	13.13
19	1.1786	22.0	35.72	223.9	1.869	13.98
20	1.1884	23.0	37.68	237.7	1.984	14.84
21	1.1984	24.0	39.68	241.7	2.100	15.71
22	1.2083	25.0	41.66	265.8	2.218	16.60
23	1.2184	26.0	43.68	280.2	2.339	17.49
24	1.2285	27.0	45.70	294.8	2.461	18.41
25	1.2387	27.9	47.74	309.7	2.584	19.33
26	1.2489	28.9	49.78	324.7	2.710	20.27
27	1.2592	29.8	51.84	340.0	2.837	21.23
28	1.2695	30.8	53.90	355.5	2.966	22.19
29	1.2800	31.7	56.00	371.2	3.098	23.17
30	1.2905	32.6	58.10	387.2	3.231	24.17
31	1.3010	33.6	60.20	403.3	3.366	25.18
32	1.3117	34.5	62.34	419.7	3.503	26.20
33	1.3224	35.4	64.48	436.4	3.642	27.24
34	1.3331	36.2	66.62	453.3	3.783	28.30
35	1.3440	37.1	68.80	470.4	3.926	29.37
36	1.3549	38.0	70.98	487.8	4.071	30.45
37	1.3659	38.8	73.18	505.4	4.218	31.55
38	1.3769	39.7	75.38	523.2	4.366	32.66
39	1.3879	40.5	77.58	541.3	4.517	33.79
40	1.3991	41.4	79.82	559.6	4.670	34.94
41	1.4103	42.2	82.06	578.2	4.826	36.10
42	1.4215	43.0	84.30	597.0	4.982	37.27
43	1.4329	43.8	86.58	616.1	5.142	38.47
44	1.4443	44.6	88.86	635.5	5.303	39.67

[8] Computed from values given in *International Critical Tables.*

TABLE VIII-3 (*continued*)

KOH, %	Sp. gr.	Baumé	Twaddell	KOH wt. in soln.		
				g./l.	lbs./gal.	lbs./cu.ft.
45	1.4558	45.4	91.16	655.1	5.467	40.90
46	1.4673	46.2	93.46	675.0	5.633	42.14
47	1.4790	47.0	95.80	695.1	5.801	43.40
48	1.4907	47.7	98.14	715.5	5.971	44.67
49	1.5025	48.5	100.50	736.2	6.144	45.96
50	1.5143	49.2	102.86	757.2	6.319	47.27
51	1.5262	50.0	105.24	778.4	6.496	48.59
52	1.5382	50.7	107.64	799.9	6.675	49.94

(2) Caustic Potash

Caustic potash, KOH, is not as important for soap manufacture as caustic soda, but it was widely used in the United States to enhance solubility during the coconut oil shortage of World War II, and is still important for this purpose. It is used for the manufacture of soft soap. Some soapmakers replace some of the caustic soda for saponification with caustic potash in order to produce by the formation of a certain percentage of potash soap a more fluid soap which is easier to work.

KOH is produced mainly by electrolysis of KCl. Smaller quantities are also produced by the action of lime, $Ca(OH)_2$, on solutions of the carbonate. KOH is even more hygroscopic than NaOH and more soluble in water. Thus, solutions of KOH in water can attain a higher percentage of KOH than solutions of NaOH (see Table VIII-3).

The usual grade of purity of high-grade technical KOH in the United States is approximately 88–92% KOH; lower grades are sold with 73–75% KOH. It is on the market as solid, in drums, as flakes, as granules and as lumps (drums of 100 ,110, 220, and 325 lbs.). As a liquid, it contains about 45% KOH and is marketed in drums; as a highly concentrated liquid of 50% KOH content it is delivered in tank cars. The technical solid product has a gray-green color; the solutions are nearly water-white. KOH has a molecular weight of 56.11; the chemically pure product is white, with a specific gravity of 2.044 and a melting point of 380°C. When exposed to air it absorbs water and carbon dioxide to form potassium carbonate K_2CO_3.

Precautions for handling KOH are the same as for NaOH. The corrosiveness of KOH solutions is, in principle, the same as that of NaOH solutions. Table VIII-3 gives added information about KOH solutions.

INORGANIC SOAP BUILDERS

Before describing the properties of soap builders, two A.S.T.M. definitions should be kept in mind when using inorganic as well as organic soap builders or fillers.

Builder. A material added to soap or synthetic detergent to improve its effectiveness under conditions of use.

Filler. A material added to soap or other detergent which does not improve its attractiveness or its effectiveness under the conditions of use.

As a matter of fact it is not easy in any case to decide whether a material added to soap actually improves the soap or if it acts only as a filler. The general tendency of present day soapmakers, however, is to add nothing to a soap that does not improve the effectiveness of the product in some way. For example, if 10% soda ash gives the maximum detergency to a certain soap mixture, then the addition of 12% could be considered as 10% builder and 2% filler.

(1) Sodium Carbonate

Sodium carbonate was produced in early times from the ashes of seaweeds (potassium carbonate was similarly obtained from the ashes of land plants), but was obtained later by the Leblanc process developed under pressure of war conditions in France at the end of the 18th century. This process was the main method of manufacture during the following 100 years. (The Leblanc process is still used to-day for the production of potassium carbonate from potassium chloride, especially in Europe.)

Sodium carbonate is produced mainly in two ways: (*1*) by the ammonia soda process (Solvay process), and (*2*) from electrolytic caustic soda.

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(1) *The ammonia soda process:* The chemical reactions in this process are as follows. Carbon dioxide passes up a tower, down which runs a brine saturated with ammonia which reacts to give sodium bicarbonate, which is then treated to give off carbon dioxide and water with the formation of the normal sodium carbonate:

$$CO_2 + H_2O + NaCl + NH_3 \rightarrow NaHCO_3 + NH_4Cl \tag{a}$$
$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \tag{b}$$

The carbon dioxide necessary for this process is usually obtained by heating calcium carbonate (limestone):

$$CaCO_3 \rightarrow CaO + CO_2 \tag{c}$$

and from the decomposition of $NaHCO_3$ (equation b). The ammonia is recovered from the ammonium chloride by reacting it with $Ca(OH)_2$ by slaking the CaO obtained by burning limestone (equation c):

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O + 2NH_3 \tag{d}$$

The process actually depends on the low solubility of sodium bicarbonate, especially in presence of excess CO_2:

$$NaCl + NH_4HCO_3 \rightarrow NaHCO_3 \downarrow + NH_4Cl \tag{e}$$

(2) The process from *electrolytic caustic soda* is used in the United States where electric power is cheap, and consists in transforming the electrolytic caustic NaOH with carbon dioxide into Na_2CO_3 (see above).

There are three distinct forms of sodium carbonate on the market:

(A) SODA ASH

Soda ash, anhydrous Na_2CO_3, a greyish-white powder. According to A.S.T.M. specification D458-9:

Soda ash shall be a high grade anhydrous sodium carbonate in powdered form and shall be of the type specified by the purchaser.

Soda ash, after drying for 1 hr. at 155° C., shall conform to the following requirements as to chemical composition:

Total alkalinity, calculated as Na_2CO_3	99.16% (min.)
Sodium bicarbonate ($NaHCO_3$)	0.5% (max.)
Matter insoluble in water	0.25% (max.)

At the place of manufacture, the loss in weight on heating 2 g. of the material at 150 to 155° C. for 1 hr. shall not exceed 1 per cent.

When the sample is taken at other than the place of manufacture, it shall be recognized that the soda ash is hygroscopic. Hence from the percentage loss in weight on heating, there shall be deducted the percentage gain in net weight of the package as sampled over the net shipping weight to arrive at the percentage loss in weight on heating at the place of manufacture.

Types of soda ash shall be designated as follows on the basis of the density as received:

Designation	Apparent volume of 30 g., ml.		Apparent density lbs./cu.ft.	
	Min.	Max.	Min.	Max.
Light	50	65	29	37
Extra-light	75	95	20	25

Unless otherwise specified in the contract, soda ash shall be purchased by net weight as packed at the place of manufacture.

(B) SODIUM CARBONATE MONOHYDRATE

Sodium carbonate monohydrate (crystal carbonate), $Na_2CO_3 \cdot H_2O$, a white powder, specific gravity 1.55. It loses water at 100 C. This product is not manufactured or used in the United States.

(C) HYDRATED SODIUM CARBONATE

Hydrated sodium carbonate, $Na_2CO_3 \cdot 10H_2O$, is also known as washing soda or soda crystals. It is a pure product, but as the cost of transportation is high the anhydrous form of sodium carbonate is more important.

(D) SODIUM SESQUICARBONATE

Sodium sesquicarbonate, or laundry soda, has the chemical composition $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ (a mixture of sodium carbonate with sodium bicarbonate). It is a white uniform powder and, according to A.S.T.M. specification D-457-39, conforms to the specifications given in Table IX-1.

TABLE IX-1

	Minimum	Maximum
Total alkalinity as Na_2O	39%	43%
Sodium bicarbonate ($NaHCO_3$)	35%	50%
Sodium carbonate (Na_2CO_3)	35%	50%
Matter insoluble in water	—	0.1%

(E) SODIUM BICARBONATE

This is used in small quantities in the soap industry, chiefly for the manufacture of powdered shampoos and as an ingredient in laundry bar soaps. It is a solid white crystalline salt of specific gravity 2.2. It loses carbon dioxide on heating to become the carbonate.

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 \uparrow$$
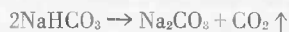
Sodium bicarbonate is sometimes used together with paraffin to superfat

toilet soap and to eliminate the effect of any free alkali or hydrolytically freed alkali on the skin.

(F) Sodium Carbonate Perhydrate

A special sodium carbonate is *sodium carbonate perhydrate*, with 14.8% active oxygen. This product is not a true peroxide, but an addition compound in which crystal water is replaced by hydrogen peroxide. It has found considerable use in the soap industry of Germany and Great Britain. In Germany, large amounts were used in the manufacture of Persil as soon as the borax shortage made the use of perborate unwise.

(2) Potassium Carbonate

Potassium carbonate, K_2CO_3, may be produced from potassium chloride by the Leblanc process, but the principal method is by carbonation of electrolytic caustic potash, or by reacting potassium chloride with magnesium carbonate in the presence of excess CO_2, producing mixed carbonates of potassium and magnesium. The insoluble magnesium carbonate is filtered from the soluble potassium carbonate.

Potassium carbonate is strongly hygroscopic, it is deliquescent. Specific gravity, 2.33. The commercial grades are 80–85%, 85–90%, 90–95%, and 96–98%, and they are usually sold in 400–800 lb. casks.

(3) Sodium Chloride and Potassium Chloride

(A) Common Salt

Common salt is very important for the soap industry as a "salting-out agent." Indirectly, salt is important for the soap industry because it is the raw material for the preparation of caustic soda.

Salt for the soap industry should be of a high grade of purity, and only small percentages of magnesium and calcium salts may be present (not more than 0.5%). Otherwise the corresponding insoluble salts of the fatty acids are formed during the salting-out process in the pan. In addition, salts with too high a content of these salts have a tendency to cake, which is very troublesome.

The chemical and physical properties of sodium chloride (NaCl) are: mol. w. 58.45, specific gravity 2.161, melting point 804°C. Table IX-5 gives the specific weight of salt solutions of different percentages.

The solubility of salt in hot water is only slightly higher than in cold water. (At 20°C., 36 parts in 100 parts water; and at 100°C., about 39 parts in 100 parts water).

TABLE IX-2

SODIUM CARBONATE—DENSITY OF AQUEOUS SOLUTIONS AT 20/4°C. [8]

Sp.gr.	Wt. of Na₂CO₃ in soln.		Cu.ft.	Na₂CO₃, %	°Bé	°Twaddell
	g./l.	lbs./gal.				
1.0086	10.09	0.08417	0.6297	1	1.2	1.72
1.0190	20.38	0.1701	1.272	2	2.7	3.80
1.0398	41.59	0.3471	2.597	4	5.6	7.96
1.0606	63.64	0.5311	3.973	6	8.3	12.12
1.0816	86.53	0.7221	5.403	8	10.9	16.32
1.1029	110.3	0.9204	6.885	10	13.5	20.58
1.1244	134.9	1.126	8.424	12	16.0	24.88
1.1463	160.5	1.339	10.02	14	18.5	29.26

Factor to convert Na_2CO_3 to Na_2O is 0.585.
Factor to convert Na_2O to Na_2CO_3 is 1.71.

TABLE IX-3

DENSITIES OF HIGHER CONCENTRATIONS OF SODIUM CARBONATE SOLUTIONS[9]

Na₂CO₃, %	Na₂O, %	Sp.gr. 30/4°C.	Temp. at which soln. is satd.		Na₂CO₃ at 30°C.		
			°F.	°C.	lb./gal.	lb./cu.ft.	g./l.
10	5.8	1.099	47.3	8.5	0.92	6.86	109.9
11	6.4	1.109	50.7	10.4	1.02	7.62	122.1
12	7.0	1.120	53.8	12.1	1.12	8.39	134.4
13	7.6	1.131	56.5	13.6	1.23	9.18	147.1
14	8.2	1.142	59.0	15.0	1.33	9.98	159.8
15	8.8	1.153	62.0	16.7	1.44	10.80	173.0
16	9.4	1.164	64.4	18.0	1.55	11.62	186.2
17	9.9	1.175	66.7	19.3	1.67	12.47	199.8
18	10.5	1.186	68.7	20.4	1.78	13.33	213.5
19	11.1	1.197	70.7	21.5	1.90	14.21	227.6
20	11.7	1.209	72.7	22.6	2.02	15.09	241.7
21	12.3	1.220	74.3	23.5	2.14	16.00	256.4
22	12.9	1.232	76.1	24.5	2.26	16.92	271.0
23	13.5	1.244	77.9	25.5	2.39	17.86	286.1
24	14.0	1.255	79.5	26.4	2.51	18.81	301.3
25	14.6	1.267	81.0	27.2	2.64	19.78	316.9
26	15.2	1.279	82.4	28.0	2.78	20.76	332.5
27	15.8	1.291	83.8	28.8	2.91	21.77	348.7
28	16.4	1.303	85.3	29.6	3.04	22.78	364.9

Na₂CO₃, %	Na₂O, %	Sp.gr. 40/4°C.	Temp. at which soln. is satd.		Na₂CO₃ at 40°C.		
			°F.	°C.	lb./gal.	lb./cu.ft.	g./l.
29	17.0	1.306	86.5	30.3	3.16	23.65	378.9
30	17.5	1.318	88.0	31.1	3.30	24.69	395.4
31	18.1	1.330	89.1	31.7	3.44	25.73	412.2
32	18.7	1.342	91.9	33.3	3.58	26.80	429.3

[9] Courtesy Solvay Process Company.

(B) Potassium Chloride

Potassium chloride is much less important to the soap industry. It is a colorless cubic crystallinic powder, or granules, with a molecular weight of 74.56, specific gravity 1.988, and a melting point of 790°C. Table IX-6 gives the specific weight of potassium chloride solutions of different percentages. The salt is used for the manufacture of soft or liquid soaps.

TABLE IX-4

Potassium Carbonate—Density of Aqueous Solutions at 20/4°C. [8]

| Sp.gr. | G./l. | Wt. of K$_2$CO$_3$ in soln. | | K$_2$CO$_3$, % | Bé | Twaddell |
		lb./gal.	lb./cu.ft.			
1.0072	10.07	0.08405	0.6288	1	1.0	1.44
1.0163	20.33	0.1696	1.269	2	2.3	3.26
1.0345	41.38	0.3453	2.583	4	4.8	6.90
1.0529	63.17	0.5272	3.944	6	7.3	10.58
1.0715	85.72	0.7154	5.351	8	9.7	14.30
1.0904	109.0	0.9100	6.607	10	12.0	18.08
1.1096	133.2	1.111	8.313	12	14.3	21.92
1.1291	158.1	1.319	9.869	14	16.6	25.82
1.1490	183.8	1.534	11.48	16	18.8	29.80
1.1692	210.5	1.756	13.14	18	21.0	33.84
1.1898	238.0	1.986	14.86	20	23.1	37.96
1.2107	266.4	2.223	16.63	22	25.2	42.14
1.2320	295.7	2.468	18.46	24	27.3	46.40
1.2536	325.9	2.720	20.35	26	29.3	50.72
1.2756	357.2	2.981	22.30	28	31.3	55.12
1.2979	389.4	3.249	24.31	30	33.3	59.58
1.3548	474.2	3.957	29.60	35	38.0	70.96
1.4141	565.6	4.720	35.31	40	42.5	82.82
1.4759	664.2	5.543	41.46	45	46.8	95.18
1.5404	770.2	6.428	48.08	50	50.9	108.08

Factor to convert K$_2$CO$_3$ to K$_2$O is 0.6809
Factor to convert K$_2$O to K$_2$CO$_3$ is 1.467

(4) The Soluble Silicates

The soluble silicates, especially sodium silicate, were for many years the most valuable builders in soap manufacture, particularly in bar soaps. Although its place in the industry is well established, decreased use of bar soaps particularly in America, and increased use of powder with their less alkaline types of builder, have somewhat reduced their overall importance, although on a tonnage basis they probably still exceed any other soap builder in use today.

Before dealing with the different types of soluble silicates now used in the soap industry, their manufacture will be discussed. Sodium silicates may be

TABLE IX-5

Sodium Chloride—Density of Aqueous Solutions at 20/4° C.[8]

Sp.gr.	Wt. of NaCl in soln.			NaCl, %	°Bé	°Twaddell
	g./l.	lb./gal.	lb./cu.ft.			
1.0053	10.05	0.08390	0.6276	1	0.8	1.06
1.0125	20.25	0.1690	1.264	2	1.8	2.50
1.0268	41.07	0.3428	2.564	4	3.8	5.36
1.0413	62.48	0.5214	3.901	6	5.8	8.26
1.0559	84.47	0.7050	5.274	8	7.7	11.18
1.0707	107.1	0.8935	6.684	10	9.6	14.14
1.0857	130.3	1.087	8.134	12	11.5	17.14
1.1009	154.1	1.286	9.622	14	13.3	20.18
1.1162	178.6	1.490	11.15	16	15.1	23.24
1.1319	203.7	1.700	12.72	18	16.9	26.38
1.1478	229.6	1.916	14.33	20	18.7	29.56
1.1640	256.1	2.137	15.99	22	20.4	32.80
1.1804	283.3	2.364	17.69	24	22.2	36.08
1.1972	311.3	2.598	19.43	26	23.9	39.44

obtained by fusing sand and sodium carbonate in a furnace (similar to those used for the manufacture of glass). The reaction product is run off from the furnace and solidified. The mass is then broken up and ground. If a solution of silicates is to be obtained, the ground material is dissolved in water under pressure in a rotary dissolver. The ease with which the silicate glass may be dissolved always varies according to the ratio of sodium oxide (Na_2O) to silica (SiO_2), which also determines the maximum concentration at which the solution is fluid enough to handle. However, solubility may be decreased

TABLE IX-6

Potassium Chloride—Density of Aqueous Solutions at 20/4° C.[8]

Sp.gr.	Wt. of KCl in soln.			KCl, %	°Bé	°Twaddell
	g./l.	lb./gal.	lb./cu.ft.			
1.0046	10.05	0.08384	0.6272	1	0.7	0.92
1.0110	20.22	0.1687	1.262	2	1.6	2.20
1.0239	40.96	0.3418	2.557	4	3.4	4.78
1.0369	62.21	0.5192	3.884	6	5.2	7.38
1.0500	84.00	0.7010	5.244	8	6.9	10.00
1.0633	106.3	0.8874	6.638	10	8.6	12.66
1.0768	129.2	1.078	8.067	12	10.3	15.36
1.0905	152.7	1.274	9.531	14	12.0	18.10
1.1043	176.7	1.475	11.03	16	13.7	20.86
1.1185	201.3	1.680	12.57	18	15.4	23.70
1.1328	226.6	1.891	14.14	20	17.0	26.56
1.1474	252.4	2.107	15.76	22	18.6	29.48
1.1623	279.0	2.328	17.41	24	20.2	32.46

by the presence of relatively small amounts of impurities. It is practically impossible to dissolve the glass by ordinary means, and, since most industrial uses require liquid grades, most of the silicates are sold in solution. Widely different grades are produced by changing the proportions of ingredients, by regulating the concentration of the solutions, and by special processes which impart specific properties.

The following equation is an example of the reaction taking place in the furnace when producing sodium metasilicate from sand (SiO_2) and sodium carbonate:

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$$

(A) THE POLYSILICATES

The qualities of silicates, either in liquid or solid form, are determined mainly by the ratio $Na_2O : SiO_2$. The range of commercial grades of silicates is between 1 : 3.90 and 3 : 2, which means a range of a silicate with low alkalinity to one of very high alkalinity. For admixture with soap for the manufacture of silicated soaps, silicates of the ratio $1Na_2O : 3SiO_2$ to $1Na_2O : 2.2SiO_2$ are preferred.

A popular brand "N" (Philadelphia Quartz Co.) of silicate for soap manufacture is of the ratio 1 : 3.22. If this is taken as a starting point for silicate solutions of different ratios, the following quantities of caustic soda solution are necessary for converting to other ratios:

PARTS OF CAUSTIC OR LYE REQUIRED TO GIVE THE INDICATED
$Na_2O : SiO_2$ RATIO WITH 100 PARTS OF "N" BRAND

Ratio $Na_2O : SiO_2$	1 : 3.0	1 : 2.8	1 : 2.5	1 : 2.2
Solid caustic (76% Na_2O), parts	0.95	1.85	3.45	5.85
"Liquid caustic" (38% Na_2O)	1.90	3.70	6.90	11.70
36% lye (NaOH)	3.07	5.98	11.23	17.93
30% lye (NaOH)	3.90	7.59	14.26	22.77

The characteristic of a number of brands of silicates for soap manufacture are as follows (Philadelphia Quartz Co.):

Brand	"N"	"K"	"U"	"C"
Sodium oxide (Na_2O), %	8.9	11.0	13.8	18.0
Silica (SiO_2), %	28.7	31.9	33.1	36.0
Water, %	62.1	57.0	52.0	46.0
Ratio $Na_2O : SiO_2$	1 : 3.22	1 : 2.90	1 : 2.44	1 : 2.00
Baumé	41	47	53	59.3

The standard method of soapmakers is to take one brand of silicate and transform it into a silicate of the desired ratio, as already described. On the

other hand, the use of a prepared alkaline silicate has several advantages:
(*1*) The soapmaker is saved the labor and other costs involved in making up
the caustic solutions to be added to the silicate. (*2*) Separate storage tanks
for causticized silicates are not required. (*3*) The proportions of Na_2O and
SiO_2 of the prepared silicates are carefully controlled. To obtain equivalent
control the soap manufacturer must analyze each mixture he makes and cor-
rect by the addition of one or the other solution as necessary. (*4*) The reac-
tion between the caustic and the silicate is slow and a period of at least 24
hours should elapse before the mixture is used. No matter how carefully
the caustic is added to the silicate, under the conditions ordinarily prevailing
in soap plants, there is usually some chance that the complete reaction will
not take place. Any silicate more siliceous than "C" Brand ($Na_2O : 2SiO_2$)
will reduce the free alkali in the soap. Causticized silicate which has not
fully reacted may introduce free alkali into the soap.

Table IX-7 gives the properties of various silicate solutions.

Fig. IX-1 gives the *p*H for silicates of soda of various $Na_2O : SO_2$ ratios.[9a]

The actual process of incorporating silicates into the soap will be described
in a later chapter.

(B) THE METASILICATES

Even if the silicates of more alkaline character are usually not incorporated
into the soap itself, they are very often used as detergents, either alone or in
combination with soap or other detergents. It is thus worthwhile to describe
some of these high alkaline silicates here.

Different types of powdered or granular silicates of a ratio 1:1 or of
greater alkalinity are on the market. Snell[10] describes the principles of the
production of silicates of the 1:1 or higher alkaline type as follows:

"A solution of sodium metasilicate of the theoretical composition deposits crystalline
hydrates when concentrated to 50 per cent. Solutions less alkaline than the metasilicate
will not crystallize, although they can be spray congealed. When crystallization occurs
from a solution more alkaline than the metasilicate, the crystals are of metasilicate, but
with each addition of alkali resulting in a lower hydrate. Thus a solution containing
10.5 grams of Na_2SiO_3, 54.5 grams of water and 40 grams of sodium hydroxide deposits
the 9-H_2O compound, but increase of the sodium hydroxide to 60 grams results in the
6-H_2O compound. The orthosilicate cannot be crystallized from solution. Substantiated
hydrated metasilicates are Na_2SiO_3, $5H_2O$; Na_2SiO_3, $6H_2O$; Na_2SiO_3, $8H_2O$ and Na_2SiO_3,
$9H_2O$. The melting points are 72.2°, 62.85°, 48.35° and 47.85° respectively. On long
heating at 100°, sodium metasilicate is dehydrated to about 1.5 molecules of combined
water.

"Basically methods of production of the hydrates are by crystallization or solidifica-
tion of the theoretical composition with the proper moisture content. This may be pro-
duced by addition of alkali to the more siliceous silicates. In solidifying the composition

[9a] C. J. Jeglum, *Chem. Industries*, *54* (Oct., Nov., 1941).

[10] F. D. Snell, *Soap*, *16*, No. 10, 29 (1940).

it is preferable to hold at a temperature just under the melting point of the desired hydrate. Trade products whether crystallized or congealed approximate the 5-hydrate.

"Sodium sesquisilicate crystallizes from a solution containing 19 per cent of Na_2SiO_3,

TABLE IX-7

SODIUM SILICATE—DENSITY OF AQUEOUS SOLUTIONS AT 20/4° C.[8]

Sp.gr.	Wt. of $Na_2O + 2.06$ SiO_2 in soln.			% Na_2O plus 2.06 SiO_2	°Be	°Twaddell
	g./l.	lb./gal.	lb./cu.ft.			
1.007	10.77	0.08404	0.6287	1	1.0	1.4
1.016	20.32	0.1696	1.269	2	2.3	3.2
1.035	41.40	0.3455	2.585	4	4.9	7.0
1.054	63.24	0.5278	3.948	6	7.4	10.8
1.073	85.84	0.7164	5.359	8	9.9	14.6
1.093	109.3	0.9122	6.824	10	12.3	18.6
1.113	133.6	1.115	8.338	12	14.7	22.6
1.134	158.8	1.325	9.911	14	17.1	26.8
1.156	185.0	1.544	11.55	16	19.6	31.2
1.178	212.0	1.770	13.24	18	21.9	35.6
1.200	240.0	2.003	14.98	20	24.2	40.0
1.223	269.1	2.245	16.80	22	26.4	44.6
1.247	299.3	2.498	18.68	24	28.7	49.4
1.271	330.5	2.758	20.63	26	30.9	54.2
1.296	362.9	3.028	22.65	28	33.1	59.2
1.321	396.3	3.307	24.74	30	35.2	64.2
1.346	430.7	3.595	26.89	32	37.3	69.2
1.371	466.1	3.890	29.10	34	39.2	74.2
1.397	502.9	4.197	31.40	36	41.2	79.4
1.423	540.7	4.513	33.76	38	43.1	84.6
1.450	580.0	4.840	36.21	40	45.0	90.0
1.520	684.0	5.708	42.70	45	49.6	104.0
1.594	797.0	6.651	49.76	50	54.0	118.8
1.673	920.2	7.679	57.44	55	58.3	134.6

Sp.gr.	Wt. of $Na_2O + 2.44$ SiO_2 in soln.			% Na_2O plus 2.44 SiO_2	°Be	°Twaddell
	g./l.	lb./gal.	lb./cu.ft.			
1.285	359.8	3.003	22.46	28	32.2	57.0
1.309	392.7	3.277	24.52	30	34.2	61.8
1.334	426.9	3.562	26.65	32	36.3	66.8
1.360	462.4	3.859	28.87	34	38.4	72.0
1.378	499.3	4.167	31.17	36	40.5	77.4
1.415	537.7	4.487	33.57	38	42.5	83.0
1.445	578.0	4.824	36.08	40	44.7	89.0

33 per cent of sodium hydroxide and the balance water. The crystallized product may be expressed as $Na_6Si_2O_7$, $11H_2O$; Na_2SiO_3, Na_4SiO_4, $11H_2O$ or Na_3HSiO_4, $5H_2O$. On heating it is altered to other compounds before reaching its metastable melting point which is around 80–90°. The melting point of the dehydrated material is about 1122°.

"Commercial sodium orthosilicate may be either a solidified anhydrous material or a congealed hydrated product. . . .

"For convenient reference Table IX-8 shows the composition of the various hydrates of the silicates expressed in terms of Na_2O, SiO_2, and H_2O with equivalent figures for soda ash and caustic soda.

"Such hydrates must be kept in tight containers as even sodium metasilicate gains or loses moisture at atmospheric pressure[11] and absorbs carbon dioxide. . . ."

A special type of metasilicate was developed under the name of Drymet.[12] As the name implies, this is a commercial dry anhydrous sodium metasilicate in powder form which is readily soluble in water. Since this type of metasilicate is anhydrous, it may be mixed with powdered NaOH to form silicate–caustic mixtures of any desired proportion. The crystalline detergent
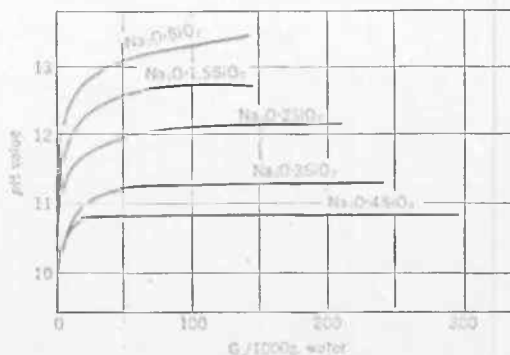
Fig. IX-1. pH curves for silicates of soda of various ratios.[9a] (Courtesy Philadelphia Quartz Co.).

silicates containing water have limited the ratio $Na_2O:SiO_2$ of solid silicates chiefly to the following types: metasilicate $Na_2O \cdot SiO_2 \cdot 5H_2O$, sesquisilicate $3Na_2O:2SiO_2 \cdot H_2O$. The only water-free silicate was the orthosilicate $2Na_2O:SiO_2$.

Detergent sodium silicates differ widely among themselves, however, in cleaning properties—especially at production speed- -and the efficiency of a detergent compound designed on a sodium silicate base is quite large determined by whether or not the base material is in optimum $Na_2O:SiO_2$ balance.

The anhydrous condition of the metasilicate makes it possible to produce mixtures of metasilicate with caustic NaOH or with any alkaline builder to give the optimum effect for the special purpose.

[11] J. G. Vail, Soluble Silicates in Industry, Reinhold, New York, 1928, p. 126.
[12] The Cowles Detergent Co., Cleveland, Ohio.

(C) Detergent Effect of Alkali Silicates

The detergent effect of alkali silicates was studied by Liddiard.[13]

Silicates form good buffering solutions in alkaline detergents and provide a means of economy in detergent consumption. The free hydroxyl ions are only released as required from the nonionized molecules in solution. Since it is the hydroxyl ion which is largely used up in cleaning processes of this kind, the fall is gradual, with a steady release of silicate ions, or of micelles of silicate ions with hydrated silica molecules. These charged bodies play a very important part in the deflocculating of solid residues, resulting in a colloidal suspension. The important thing is that the action is reversible; as the hydroxyl ions are removed, more are forthcoming from the hydrolysis of the silicate.

TABLE IX-8

Composition of Higher Silicates and Known Hydrates with NaOH and Na_2CO_3 for Comparison[10]

	Na_2O	SiO_2	H_2O
NaOH	77.5	—	22.5
Na_4SiO_4	67.4	32.6	—
$Na_6Si_2O_7$	60.8	39.2	—
$Na_6Si_2O_7 \cdot 11H_2O$ $(Na_3HSiO_4 \cdot 5H_2O)$	36.9	23.8	39.3
Na_2SiO_3	50.8	49.2	—
$Na_2SiO_3 \cdot 5H_2O$	29.3	28.5	42.2
$Na_2SiO_3 \cdot 6H_2O$	26.9	26.1	47.0
$Na_2SiO_3 \cdot 8H_2O$	23.3	22.5	54.2
$Na_2SiO_3 \cdot 9H_2O$	21.9	21.1	57.0
Na_2CO_3	58.5	—	—

The great difficulty in the practical use of the silicates is their high alkalinity when employed in the proper ratio to yield good detergent solutions. For a detailed discussion of the detergent effect of silicates and other builders, see Chapter XXX.

Among the methods of studying the surface activity of compounds is the measurement of contact angle against some particular surface. The wetting of a wax deposit by alkaline solutions has been studied and the contact angles measured. These are given in Table IX-9 for solutions equivalent to 1% of Na_2O, against a paraffin wax surface at 18°C.

These values show caustic soda and other alkaline salts to be very poor wetting agents for paraffin wax as compared to the silicates, and indicate the efficiency of the latter material in the cleaning of metal surfaces, etc.

[13] P. D. Liddiard, *Chem. Age*, *51*, 317–20 (1944) through *Soap*, *20*, No. 12, 63 (1944).

(D) ASTM SPECIFICATIONS FOR METASILICATES

The ASTM specification for sodium metasilicate (Designation D537-41) and sodium sesquisilicate (Designation D504-41) are given here in an abridged form. It will be noted that the ASTM Specifications deal with the meta- or sesquisilicates in their crystalline form.

1. These specifications for *sodium metasilicate* cover materials suitable for various washing, cleaning, and scouring processes, with or without soap as conditions demand, and where a moderately strong alkaline material is desired.

2. Sodium metasilicate shall be a white uniform product in either granular or crystalline form as specified by the purchaser.

TABLE IX-9

Alkaline compound	Contact angle, degrees
Liquid silicate, $Na_2O : SiO_2$, $1 : 3.3$	Less than 10
Liquid silicate, $Na_2O : SiO_2$, $1 : 2$	40.5
Sodium metasilicate	54.0
Sodium sesquisilicate	54.5
Sodium orthosilicate	55.5
Trisodium phosphate	70.0
Sodium carbonate	102.0
Sodium hydroxide	104.0

3. Sodium metasilicate, as received, shall conform to the following requirements as to chemical composition:

	Minimum	Maximum
Sodium metasilicate, calc. as $Na_2SiO_3 \cdot 5H_2O$, %	98.0	—
Total alkalinity as Na_2O, to methyl orange, %	28.5	30
Total silica as SiO_2, %	27.5	29
Matter insoluble in water, %	—	0.2

4 (a). Sodium metasilicate shall be purchased by net weight, but in the event of weight shortage it shall be recognized that sodium metasilicate is subject to a possible gain or loss of weight due to atmospheric or storage conditions, or both. Therefore, the calculation of net weight shall be based upon a product containing 98% of sodium metasilicate (calculated as $Na_2SiO_3 \cdot 5H_2O$). The net weight of the material to be paid for shall be calculated as follows:

$$W = R \times T/98$$

where W = net weight of the material to be paid for, R = net weight of material as received, and T = total sodium metasilicate calculated as $Na_2SiO_3 \cdot 5H_2O$.

4 (b). In the event that the calculation under paragraph 4 (a) results in a figure greater than 100%, the seller waives the right to invoice the purchaser for any amount in excess of 100%.

1. These specifications for *sodium sesquisilicate* cover material suitable for various washing, cleaning, and scouring processes, with or without soap as conditions demand, and where a strongly alkaline material is desired.

2. Sodium sesquisilicate shall be a light-colored, uniform, granular product and shall be furnished in airtight containers.

3. Sodium sesquisilicate, as received, shall conform to the following requirements as to chemical composition:

	Minimum	Maximum
Sodium sesquisilicate, calc. as $3Na_2O \cdot 2SiO_2 \cdot 11H_2O$, %	97.0	—
Total alkalinity as Na_2O, to methyl orange, %	35.5	37.5
Total silica as SiO_2, %	22.5	—
Matter insoluble in water, %	—	0.2

4. Sodium sesquisilicate shall be purchased by net weight.
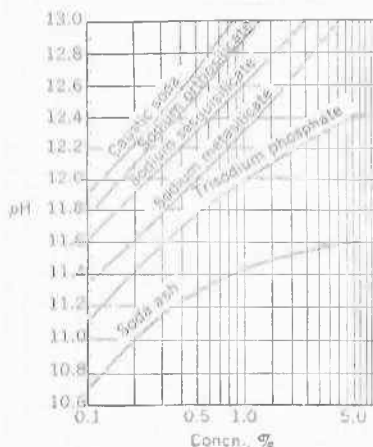
Fig. IX-2. The pH of various alkali solutions charted according to per cent concentrations[9a] (Courtesy Philadelphia Quartz Co.).

Sampling and analyzing of these materials should be carried out in accordance with ASTM methods, which will be described in Volume II. The crystalline sodium metasilicate $Na_2O \cdot SiO_2 \cdot 5H_2O$ or $Na_2SiO_3 \cdot 5H_2O$ has a melting point of 71.8°C. and the anhydrous metasilicate $Na_2O \cdot SiO_2$ (Na_2SiO_3) has a melting point of 1088°C.

At this stage it would be interesting for the reader to compare the pH values of different silicates with that of trisodium phosphate and soda ash (Fig. IX-2).

(E) POTASSIUM SILICATES

The potassium silicates are much less important for the soaper than the sodium silicates. Even for the manufacture of a "filled" soft potash soap, sodium silicate may be used instead of potassium silicate, but in this case potassium silicate has the advantage that the character of a potassium soap remains unchanged. For filling of "figged" soft soap with silicates *only* potassium silicate can be used. In addition, potassium silicate has many advantages for the manufacture of liquid soap.

The manufacture of potassium silicate is, in principle, the same as the manufacture of sodium silicate, the corresponding potassium compounds being used instead of sodium compounds. Because of the relative scarcity of potassium salts, potassium silicates are more expensive than the sodium silicates. The most usual form of potassium silicate for the soap industry is a solution of about $K_2O:2SiO_2$. A typical analysis (Philadelphia Quartz Co.) is:

K_2O	12.70%
SiO_2	25.99%
H_2O	60.83%
Heavy metals	0.30%
Ratio $SiO_2 : K_2O$	2.04

A potassium disilicate $(K_2O:2SiO_2)$ and a trisilicate $(K_2O:3SiO_2)$ are also on the market.

(5) Alkali Phosphates

The alkali phosphates have long been used as soap building materials. Within the past fifteen years, however, there have been developed a number of new type complex phosphates of low pH values having very high lime soap sequestering power, which have practically displaced the trisodium salt entirely as soap-building material, although the latter still functions in a wide variety of industrial cleaning operations and as a water softener, as already mentioned. The sodium phosphates are manufactured by reacting Na_2CO_3 and or $NaOH$ with phosphoric acid, H_3PO_4. The manufacture of trisodium phosphate, $Na_3PO_4 \cdot 12H_2O$, is given as an example.

(A) TRISODIUM PHOSPHATE (TSP). ASTM SPECIFICATIONS

The reaction of phosphoric acid and sodium carbonate forms the disodium phosphate:

$$H_3PO_4 + Na_2CO_3 \rightarrow Na_2HPO_4 + CO_2 + H_2O$$

The third hydrogen is neutralized with the caustic soda solution, with the formation of trisodium phosphate:

$$Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O$$

Trisodium phosphate, $Na_3PO_4 \cdot 12H_2O$, is a colorless crystalline powder, having a specific gravity of 1.644 and a melting point of 73.4°C. Anhydrous Na_3PO_4 is a colorless powder with specific gravity 2.537 and melting point 1340°C.

Anhydrous trisodium phosphate (TSP) slowly absorbs water from the air, resulting in a considerable increase in volume because of the great difference in specific gravity of the anhydrous and crystalline TSP. Therefore, the anhydrous TSP should be stored in closed containers protected from humidity variations.

The solubility of trisodium phosphate in water is roughly 10% by weight of Na_3PO_4 at 20°C. and 45% at 100°C. The A.S.T.M. Specification for trisodium phosphate (D538-44 abridged) is as follows:

1. These specifications cover material suitable for various washing, cleaning, and scouring processes, with or without soap as conditions demand, and where a moderately strong alkaline material is desired.

2. Trisodium phosphate shall be a white uniform product in either flake, granular, or crystalline form as specified by the purchaser.

3. Trisodium phosphate, as received, shall conform to the following requirements as to chemical composition:

	Minimum	Maximum
Trisodium phosphate, calc. as $Na_3PO_4 \cdot 12H_2O$, from P_2O_5, %	97	—
Total alkalinity as Na_2O, to methyl orange, %	16	19
Phosphoric anhydride (P_2O_5), %	18.1	—
Matter insoluble in water, %	—	0.1

4 (a). Trisodium phosphate shall be purchased by net weight but in the event of weight shortage it shall be recognized that trisodium phosphate is subject to a possible gain or loss of weight due to atmospheric or storage conditions, or both. Therefore the calculation of net weight shall be based upon a product containing 97 per cent of trisodium phosphate (calculated as $Na_3PO_4 \cdot 12H_2O$ from the determined P_2O_5). The net weight of the material to be paid for shall be calculated as follows:

$$W = R \times T/97$$

where W = net weight of the material to be paid for, R = net weight of material as received, and T = total trisodium phosphate calculated as $Na_3PO_4 \cdot 12H_2O$.

4 (b). In the event that the calculation under paragraph 4 (a) results in a figure greater than 100 per cent, the seller waives the right to invoice the purchaser for any amount in excess of 100 per cent.

(B) TETRASODIUM PYROPHOSPHATE (TSPP). ASTM SPECIFICATIONS

This important sodium phosphate is derived from the disodium phosphate by controlled dehydration as follows:

$$2NaHPO_3 \xrightarrow{\text{heat}} Na_4P_2O_7 + H_2O$$
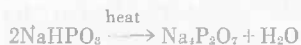
Sodium pyrophosphate exists either in a crystalline form as $Na_4P_2O_7 \cdot 10H_2O$ or in an anhydrous granular or powder form. The anhydrous form is the more common.

The A.S.T.M. Specifications (D595-45) for this compound are:

1. These specifications for tetrasodium pyrophasphate (anhydrous) cover material suitable for various washing, cleaning, and scouring processes with soap or other detergents, where a mildly alkaline material, with appreciable water softening properties, is desired.

2. Tetrasodium pyrophosphate (anhydrous) shall be a white uniform product in either granular or powdered form as specified by the purchaser.

3. Tetrasodium pyrophosphate (anhydrous), as received, shall conform to the following requirements as to chemical composition:

Tetrasodium pyrophosphate, calc. as $Na_4P_2O_7$, %   97.5* (min.)
Matter insoluble in water, %   0.20 (max.)

4 (a). Tetrasodium pyrophosphate (anhydrous) shall be purchased by net weight. When, however, due to hygroscopicity the tetrasodium pyrophosphate content is less than 97.5 per cent, a corresponding gain in weight of the package shall be expected, and the net weight shall be based on a product containing 97.5 per cent of tetrasodium pyrophosphate. The net weight of the material to be paid for shall be calculated as follows:

$$W = R \times T / 97.5$$

where W = weight of the material to be paid for, R = net weight of material as received, and T = total tetrasodium pyrophosphate calculated as percentage of $Na_4P_2O_7$.

4 (b). In the event that the calculation under paragraph 4 (a) results in a figure greater than 100 per cent, the seller waives the right to invoice the purchaser for any amount in excess of 100 per cent.

5. Material which has picked up sufficient water, as indicated by loss on ignition, to reduce the tetrasodium pyrophosphate content to 95 per cent or lower, may be rejected at the option of the purchaser.

(C) Properties of Trisodium Phosphate and Tetrasodium Pyrophosphate in Solution

Gillet[14] reported on the properties of the main orthophosphate, trisodium phosphate (TSP).

It is an alkaline salt which, in 1% solution, yields a pH of 12 at room temperature. It lends a slippery feeling to water and increases its wetting power. It has considerable emulsifying power, although the emulsions are not ordinarily permanent. It has certain specific dissolving power, but the most obvious and probably the most valuable function it performs is that of softening water.

Like soap, trisodium phosphate is a water softener, and its action is like

* When the sample is taken at other than the place of manufacture, it shall be recognized that tetrasodium pyrophosphate (anhydrous) is slightly hygroscopic. In the case of shipments in which the tetrasodium pyrophosphate content is less than 97.5 per cent, reference should be made to Section 5.

[14] J. M. Gillet, *Soap*, *15*, No. 1, 25, 26, 69 (1939).

that of soap. Each combines with the soluble calcium and magnesium salts in hard water to form insoluble compounds. The calcium and magnesium salts of soap, however, are slimy, sticky materials that adhere to textile fibers, washing machines, and anything else with which they come in contact (see Chapter XXXIII, 1).

As stated, when trisodium phosphate reacts with the calcium and magnesium in hard water, it converts them into insoluble calcium and magnesium phosphates. These phosphates drop out of solution and on standing gradually settle to the bottom of the container. They are not sticky or slimy, and do not adhere to the fibers. The calcium and magnesium are blocked out, so to speak, and cannot interfere with the foaming or detergency of soap.

This effect gradually wears off because the calcium phosphates are more soluble than the calcium soaps, and, in time, the insoluble soaps form at the expense of the phosphates.

Trisodium phosphate present in built soaps is in the form of crystals (containing about 54% water of crystallation) which are readily soluble and tend to dissolve more quickly than does the soap. In combination with soap, trisodium phosphate exhibits all the cleansing properties that characterize its use without soap, and has, as well, other values as an aid to soap: it neutralizes acid-acting substances which might react with the soap and liberate free fatty acids; it tends to repress the adsorption of soap on the fibers of goods being washed, and thus conserves the soap for surface tension phenomena and sudsing. Trisodium phosphate is particularly valuable in those territories where hard water is common. However it should always be borne in mind, that trisodium phosphate is very strongly alkali, which fact limits its use to "heavy duty" soap or detergent powders.

(D) Tetrasodium Pyrophosphate

The properties of sodium pyrophosphate (TSPP), $Na_4P_2O_7$, are in some respects quite different from those of the orthophosphate.[14] TSPP has a powerful peptizing action and a marked specific solvent action on certain organic materials such as gums and waxes. It has a strong sequestering power for iron dissolved in water, and has a colloidal effect upon the soap, which can be observed in the increase of the lathering power and detergency of the soap.

To *peptize* means to impart to minute particles of solid matter a tendency to repel each other so that small particles do not coalesce and form larger particles. This can be demonstrated by dissolving a mixture of trisodium phosphate and sodium pyrophosphate in hard water, for example, 80 parts of trisodium phosphate and 20 parts of the pyrophosphate. If trisodium phosphate alone is used, a fine precipitate forms which, on standing, tends to coagulate into larger particles and eventually settles to the bottom of the container,

leaving a clear, soft water above. In the presence of the pyrophosphate, however, the precipitate that forms at certain concentrations does not settle on standing and does not clear up. This is because the small particles of insoluble phosphate are peptized and remain in suspension.

Pyrophosphate has the power to keep iron in solution and to dissolve iron oxide that has been freshly deposited on fabrics. It is found, for example, that, if iron oxide in hydrated form is digested at 40°C. for one hour, in water containing sodium pyrophosphate, 1 g. of ferric oxide will be dissolved for each 4 g. of anhydrous sodium pyrophosphate in the solution. This means that, wherever wash water contains iron, the presence of pyrophosphate will tend to prevent it from depositing in and discoloring the goods being washed; in many cases, this makes all the difference between white clothes and yellow clothes. This is important for household washing, for laundries, and in industrial plants where the discoloration by iron is always a difficult problem to overcome. Soaps containing sodium pyrophosphate, therefore, are especially effective in these iron water districts.

In soft, iron-free water the effect of these phosphates has no marked effect on the detergent effect of soap, but in hard and/or iron-containing water the effect of pyrophosphate is easily noticeable. It is interesting to note that the pyrophosphates have a softening effect much stronger for magnesium salts than for calcium salts. The same interesting phenomenon will be seen again when we have to deal with some special phosphates later on.

At pH 10.2, the normal pyrophosphates are stable in solution over long periods of time and hydrate to the orthosphosphate very slowly, even at elevated temperatures. Increasing the alkalinity retards this reversion, while decreasing it increases the rate of conversion. This makes possible the incorporation of the pyrophosphates with soaps in the kettle or in the crutcher and long storage on the shelves without a measurable loss or effectiveness due to hydration.

It is of great advantage in many cases to use tetrasodium pyrophosphate (TSPP) as well as trisodium phosphate (TSP) in combination with water glass as a soap builder. The results of a series of washing tests with soap with 10–15% TSPP in combination with about equal or 1.5 parts of sodium silicate (1:3.25 $Na_2O:SiO_2$ calculated as anhydrous) are summarized as follows:[15]

(1) Tetrasodium pyrophosphate, when it constitutes 10–15% of the soap mixture, saves soap to the extent of 20–30% by completely preventing the magnesium ion (in unsoftened water) from precipitating soap. At higher level a partial elimination of the calcium ion also results.

(2) It reduces the insoluble soap content of the wash water by 20–30% because it reduces the magnesium and calcium ion content of the solution to this amount.

[15] J. Janota and H. H. Hull, *Oil & Soap*, 17, 96–100 (1940).

(3) Because of these facts, more soap is made available for washing and dispersing the solids and less insolubles are present to complicate dirt removal, resulting in better washing solutions at no additional cost.

In another paper[16] the detergent properties of TSP and TSPP were again investigated thoroughly. Combinations with silicates of different composition in different proportions of TSP and TSPP were tested. A general conclusion from these papers is that TSP and TSPP greatly improve the detergent efficiency of built soap-containing silicate. For a more detailed discussion of the detergent efficiency of builders, see Chapter XXX.

Another valuable property of the pyrophosphate ion is its influence on the decomposition of hydrogen peroxide solutions, which it stabilizes quite appreciably, exerting its maximum effect at pH values between 9 and 10. Tetrasodium pyrophosphate, $Na_4P_2O_7$, is therefore employed frequently in the bleaching of woolen goods with hydrogen peroxide, or with the equivalent sodium peroxide and sulfuric acid (see Chapter XIII, 3).

To complete this section on tetrasodium pyrophosphate Table IX-10 is given showing interpolated solubility values.[17]

TABLE IX-10

Temp., °C.	0	20	40	60	80	100
$Na_4P_2O_7$, g./100 g. H_2O	2.2	5.5	10.9	25.6	56.7	43.5
$Na_4P_2O_7$, % by wt. in satd. soln.	2.2	5.2	9.8	19.7	36.2	30.3

A special pyrophosphate is *sodium pyrophosphate perhydrate* with 9.0% active oxygen. This product, which is not a pure peroxide but an addition compound holding hydrogen peroxide in partial replacement of water of crystallization, is of potential interest as an addition to soap because of its water-softening properties. At the same time, active oxygen becomes available from such a soap or its solution.

(E) SODIUM HEXAMETAPHOSPHATE

Sodium hexametaphosphate, $(NaPO_3)_4$, molecular weight 611.82, which is usually available in the form of slowly dissolving glassy plates or rapidly dissolving thin flakes, is made commercially by fusing monobasic orthophosphate (NaH_2PO_4) and cooling quickly:

$$6NaH_2PO_4 \rightarrow (NaPO_3)_6 + 6H_2O$$

Of course the water evaporates during fusion. As mentioned earlier, sodium hexametaphosphate (or Graham's salt) is used for water softening,

[16] J. C. Harris, J. R. Eck, and W. W. Cobbs, *Oil & Soap, 17*, No. 1 (1940); *Oil & Soap, 19*, No. 1, 3–13 (1942).

[17] H. Menzel and L. Sieg, *Zt. Elektrochem., 38*, 283 (1932).

but it also is useful in the soap and detergent industry because it has a strong sequestering effect on the calcium and magnesium salts in ordinary water. The water is, in a sense, not actually softened by removing the calcium or magnesium salts as precipitates, but the alkaline earths are prevented from flocculation or precipitation (*e.g.*, with soap) by the use of metaphosphate. The water is "normalized." This "sequestering" property of metaphosphate distinguishes it from trisodium phosphate, which precipitates the calcium and magnesium salts as insoluble phosphate. Whereas trisodium phosphate softens water by removing these impurities as insoluble precipitates, metaphosphate holds them as soluble complexes which have no detrimental action. Thus, a washing solution containing soap and metaphosphate in hard water is as clear as a solution of distilled water and soap.

By the use of sodium metaphosphate, the problem of insoluble soaps is eliminated, for since no curds are formed in the solution, none can adhere to the fibers nor to the washing equipment.[18] It is often used in laundry work to rinse goods which may have picked up some insoluble calcium or magnesium soap from the wash solution. This rinse then removes the insoluble soaps from the fabric. It is self evident from these properties that hexametaphosphate has many advantages that make it a valuable ingredient for incorporating in washing soap cakes or soap powder.

Sodium hexametaphosphate has a *p*H of 6.7 in 1% aqueous solution, but it can be used with alkaline soap builders and/or soap at a *p*H of 8.5. At low *p*H values, or at values over 8.5, it slowly reverts to the orthophosphate and loses the sequestering power. It is this instability that prevents its large-scale use in soap products; however, it is used chiefly as a separate adjunct to them.

(F) SODIUM TETRAPHOSPHATE

Another type of sodium phosphate is the anhydrous sodium salt of tetraphosphoric acid, $Na_6P_4O_{13}$,[19] formed by heating mono- and disodium phosphates together:

$$2NaH_2PO_4 + 2Na_2HPO_4 \rightarrow Na_6P_4O_{13} + 3H_2O$$

It contains, theoretically, 39.6% Na_2O, and 60.4% P_2O_5. It is a noncrystalline glassy substance sold to the detergent industry as beads. Specific gravity of the glass is 2.55; the approximate fusion point is 600°C. The compound is permanently stable in its dry form, but it is slightly hydroscopic and absorbs moisture from the air.

In contrast to sodium hexametaphosphate, sodium tetraphosphate is a mild alkali and has a *p*H of 7.9 in 1% solution.

[18] J. M. Gillet, *Soap, 15,* No. 1, 69 (1939).
[19] We are indebted to Messrs. Rumford, Chemical Works, for their permission to use some information contained in their publications.

The comparative pH of polyphosphate solutions at 25°C. is shown in Fig. IX-3.

The effect of $Na_6P_4O_{13}$ on calcium and magnesium is in a sense similar to that of metaphosphates; it both sequesters alkaline earths and keeps them in solution. Besides, it has a sequestering power upon heavy metals such as iron, nickel, etc.; this property is important for laundry work.

In solution, $Na_6P_4O_{13}$ has stability properties similar to those of the metaphosphate class; depending on the lower or higher temperature of the solution; it slowly reverts to the orthophosphate salts. Higher temperatures hasten this process of reversion, as do alkaline salts. But in ordinary washing solutions, $Na_6P_4O_{13}$ retains its sequestering power for calcium and magnesium, even at about 65°C. for 30–40 hours.

Concn., % solids
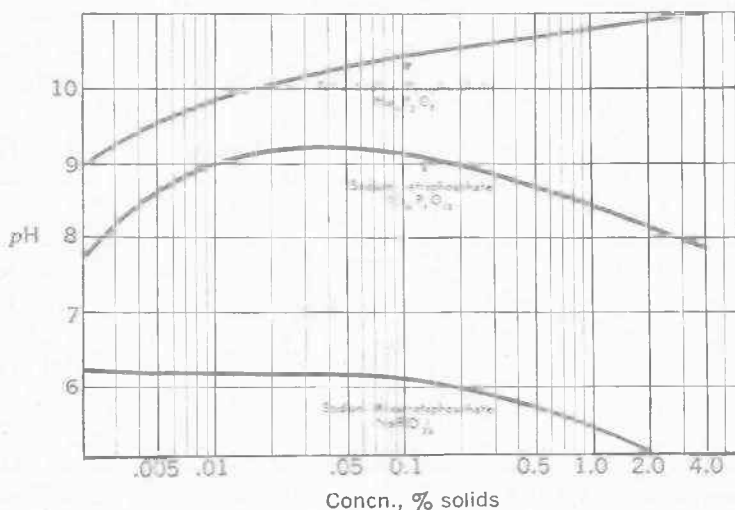
Fig. IX-3. pH of polyphosphate solutions at 25°C. (Courtesy Rumford Chemical Works.)

(G) Sodium Tripolyphosphate (STPP)

This phosphate is by far the most important developed to date as a builder for detergent products because of its high lime soap sequestering power coupled with its low pH of 9.7 in a 1% aqueous solution. It is of particular use in synthetic detergents where the builder plays a more important role than it does in soap-base products. It is formed by controlled dehydration of a mixture of mono- and disodium phosphates according to the reaction:

$$2Na_2HPO_4 + NaH_2PO_4 \rightarrow Na_5P_3O_{10} + 2H_2O$$

STPP is relatively nonhygroscopic, accordng to the data of Trexler.[20]

[20] M. V. Trexler, *Soap & Sanit. Chem.*, XXVI, No. 7, 40, 41 (1950).

Sodium tripolyphosphate sequesters lime soap by precipitation, similarly to the action of TSPP and TSP and unlike the complex-forming reaction of the hexametaphosphates. It is a better sequestering agent for Ca^{++} than is tetrasodium pyrophosphate, but slightly inferior to it in sequestering Mg^{++}.

Cold water solubility is excellent. Some data from the above reference follows:

Formula	$Na_5P_3O_{10}$
Mol. wt.	367.9
pH of 1% soln.	9.7
P_2O_5 (theor.)	57.9
Solubility	
at 25° C., wt. %	15.3
at 60° C., wt. %	16.2

(H) POTASSIUM TETRAPYROPHOSPHATE AND POTASSIUM TRIPOLYPHOSPHATE

To conclude our description of alkali phosphate soap builders we want to mention *tetrapotassium pyrophosphate*, $K_4P_2O_7 \cdot 3H_2O$ (mol. wt. 384.39), which is the only potassium phosphate that has found important use as an addition to liquid soaps and shampoos. It is a very hygroscopic salt and must be stored in closed containers.

The effect of potassium tetropyrophosphate is in principle the same as that of tetrasodium pyrophasphate. Its ready solubility and its closer relation to potassium soaps makes it especially suitable for liquid soaps. The potassium salt of the tripolyphosphate, $K_5P_3O_{10}$ can be prepared, but its uses are still under investigation.

(6) Borax

Borax serves as a mild detergent.[21] Chemically, it is $Na_2B_4O_7 \cdot 10H_2O$.

Formerly, the borax supply of the United States was derived principally from the minerals borax, colemanite, and ulexite. Most of this supply is now obtained from the mineral kernite (also called rasorite), which occurs in large deposits in Kern County, California. Kernite is sodium tetraborate with only 4 molecules of water of crystallization ($Na_2B_4O_7 \cdot 4H_2O$). The material is mined and dissolved in water; the solution is filtered to remove clay; and the water is allowed to evaporate until recrystallization takes place. Owing to the greater content of water of crystallization, about 1.4 tons of pure borax can be produced from 1 ton of pure kernite.

Specifications require that the detergent grade shall contain not less than 99.0% borax calculated on the above formula and should be entirely soluble in water. Specific gravity is 1.69.

A very important quality for some special purposes in the soap industry is

[21] F. W. Smither, *Washing, Cleansing and Polishing Materials*, U. S. Dept. of Commerce, Circular C424, Washington, 1939, p. 23.

its solubility in glycerine, and its dermatological properties in combination with soap (see Chapter XX, 3). Borax is used in combination with powdered toilet soap in dispensers, usually in a proportion of 1 part anhydrous soap to 3 parts of borax.[22] It finds wide application in cosmetics, soaps, shampoos, shaving soaps etc. Borax also has water-softening properties.

(7) Sodium Perborate

Sodium perborate, $NaBO_2 \cdot 3H_2O \cdot 1H_2O_2$ (less correctly $NaBO_3 \cdot 4H_2O$), is on the market as white granules or as a crystalline powder. It decomposes on exposure to heat and moisture when the oxygen of the hydrogen peroxide contained in the molecule is released. This release of oxygen makes the compound useful as a bleaching agent (see Chap. XXVI). On the Continent, especially in Germany, it is widely used as an addition to soap powder—up to 10% which corresponds roughly to $0.9–1\%$ available oxygen. But it is also used in the United States for special detergents, toilet preparations, dental compositions, and special shampoos. Sodium perborate is listed in the *Pharmacopoeia of the United States*, which specifies a content of not less than 86.5% of $NaBO_3 \cdot 4H_2O$, or about 9% available oxygen.

The modern German process for the production of sodium perborate has two stages. In the first stage, borax and sodium carbonate are dissolved in water to the proper concentration to yield the simple sodium borate $NaBO_2 \cdot 4H_2O$. In the next stage this solution is electrolyzed under carefully controlled conditions and hydrogen peroxide is formed by anodic oxidation which combines with the molecule of $NaBO_2 \cdot 4H_2O$ to form $NaBO_2 \cdot 4H_2O \cdot 1H_2O_2$.

It must be mentioned here that the use of sodium perborate as a mild bleaching agent in soap powder has the advantage that after the oxygen has been released the remaining sodium borate has detergent properties of its own.

The problem is to incorporate sodium perborate into soap powder so that it remains stable for a period of at least six months (see Chapter XXVI).

Sodium perborate has important qualities which make it a very convenient laundering agent. It has no appreciable deleterious effect on animal fibers such as wool and silk, and yet bleaches. It is more effective in warm or hot solutions than in the cold. But treatment in the cold is imperative for silk in spite of the lesser bleaching effect. Sodium perborate is very effective for removing stains from goods containing vegetable or synthetic fibers as cotton, linen, rayon, etc., and it has special advantage in the case of dyed goods or fabrics. The following product by J. G. Spiegler (U. S. Patent No. 2,367,-971) is described in which borax and hydrogen peroxide are combined with sodium silicate to produce "sodium perborosilicate."

[22] Federal Specification P-S-628.

The perborosilicate is produced by mixing 38° Bé caustic soda (6 parts), 36° Bé sodium silicate (22 parts), and borax (28 parts by weight). This mixture is then added to 36° Bé sodium silicate (22 parts), and 30% hydrogen peroxide (22 parts by weight). The combined mixture is stirred vigorously until it becomes gelatinous. After drying in a drier at 70–80° C., or for several days in air, the mass is finely ground.

Sodium perborosilicate is a washing and cleaning agent, and may be mixed with powdered soap for this purpose.

(8) Bentonite, etc.

A soap builder of quite different type is the natural clay product *bentonite*, first used by the Indians. The early pioneers were told by the Indians that a peculiar claylike material found in the Black Hills region of Wyoming and South Dakota was effective for cleaning and laundering clothes. These early pioneers obtained this material from "soap holes," which resulted from the wetting of the surfaces of bentonite outcroppings. This material was called "mineral soap" or "soap clay" because of its resemblance to soft soap.

Since it is derived from natural clay sources and is not a definite chemical compound, the composition of bentonite varies. Its main constituent is aluminum silicate (80–90%). The special colloidal properties have introduced it in the U. S. *Pharmacopoeia.* Bentonite is a very fine, odorless, tasteless, and practically colorless powder, free from grit. It also occurs as small granules. It is insoluble in water, but swells to about eight times its volume when added to water, and produces an opalescent suspension or paste.

The *p*H of bentonite is very near or even corresponds to ordinary detergent and soap solution. It has a certain base exchange property and softens water to a certain extent. Its emulsifying properties make it a valuable addition to soap in many cases,[23] such as for hand soap cakes for factory and garage use, and for dishwashing and scouring powder compounds in combination with abrasives.

More general use of bentonite as a detergent is described by Hirshmann and Bechtner:[24]

"Soap creates a suds, which floats away the soil; bentonite forms gels, which perform the same service. The ability of bentonite to carry particles of solid matter in aqueous suspension is one of its outstanding characteristics, widely used in other commercial processes. . . .

"Soap and bentonite both emulsify oil and grease, mineral as well as vegetable. . . .

"Soap holds carbon or dirt in suspension by its deflocculating or wetting action (which is also the cause for its sudsing). Bentonite also holds dirt in suspension because of its polarity, by which each microscopic particle of it picks up a similar speck of dirt, keeps it in suspension, prevents it from coagulating with other specks, and carries it away from the article to be cleaned. . . .

[23] M. A. Lesser, *Soap, 21,* No. 10, 37–40 (1945).
[24] W. B. Hirshmann and P. Bechtner, *Soap, 14,* No. 10, 24–26, 105 (1938).

"Soap, alkalies and a proper grade of bentonite all mix readily with water . . . once the dirt is loosened, they all prevent its re-deposition."

Mention must be made of the fact that if lime soap has formed in the wash water, bentonite has the capacity of absorbing such insoluble soaps, thus keeping them from precipitating. Formulas of different soaps containing bentonite are included in the corresponding chapter of this text.

La Rocca and Burlage[25] made a very interesting study of the suspending properties of bentonite. After discussing the identification test for bentonite in the U. S. *Pharmacopoeia* (XII) and presenting an improved stability test, the following conclusions were reached in regard to the suspending properties of the material:

TABLE IX-11

TYPICAL COMPOSITION OF TALC, KAOLIN, AND BENTONITE[26]

Substituent	Normal talc	Normal kaolin	American bentonite	Italian bentonite
Silica (SiO_2), %	51–62	47–55	67–69	69–73
Alumina (Al_2O_3), %	1.2–7	31–37	17–19	14–17
Iron oxide (Fe_2O_3), %	0.2–1.3	0–2	3.8–4.5	0.7–0.9
Magnesium oxide (MgO), %	32–35	0.2–0.5	0.5–0.6	4–1
Sodium or potassium oxide $(Na_2O$ or $K_2O)$, %	—	0.6–4	1.3–1.5	0.6–1
Calcium carbonate $(CaCO_3)$, %	Traces	Traces	0.9–1.1	2–3.6
Water, %	2–5	8–15	6–8	6–10

(1) The unusual suspending properties of bentonite are due, chiefly, to its singular latticelike crystalline structure and only to a minor degree to its small particle size.

(2) Since kaolin and fuller's earth do not exhibit this latticelike structure, they are distinctly inferior to bentonite as a suspending agent.

(3) The *p*H of the outer phase has a marked effect on the stability of clay suspensions, which, particularly in the case of bentonite, are more stable in neutral and alkaline mediums than in acid mediums.

As the valuable properties of bentonite cannot be attributed to common china clay, talc, or chalk (see Table IX-11[26]), these products, which are sometimes used as soap fillers, cannot be recommended as general additives to soap. Only in the case of scrubbing soap or special cleaners where abrasives are used as well, may these products find their use (see Chapter XX, 3). However even high grade bentonite should only be used for abrasive soaps or for soaps for laundering overalls and the like. Experiments have shown that bentonite is absorbed by the fiber.

[25] J. La Rocca and H. M. Burlage, *J. Am. Pharm. Assoc., 34,* 302–305 (1945).
[26] A. Mantagrin, *Manuel du Savonnier,* 2nd ed., Gauthier-Villars, Paris, 1946, p. 253.

(9) Ammonia

Ammonia (NH_3), a colorless gas of pungent odor, is used in the soap industry as an aqueous solution (NH_4OH) for special cleaners. It is rather seldom that it is used as the sole alkali for saponification. Only fatty acids can be saponified with ammonia, not neutral fats and oils. It is usually sold as a concentrated solution containing 28–29.5% NH_3. Table IX-12[27] shows the physical properties of ammonia solutions of different concentrations. It

TABLE IX-12

AQUA AMMONIA[27]

° Be	Sp.gr.	% NH	° Be	Sp.gr.	% NH_3	° Be	Sp.gr.	% NH
10.00	1.0000	.00	16.50	.9556	11.18	23.00	.9150	23.52
10.25	.9982	.40	16.75	.9540	11.64	23.25	.9135	24.01
10.50	.9964	.80	17.00	.9524	12.10	23.50	.9121	24.50
10.75	.9947	1.21	17.25	.9508	12.56	23.75	.9106	24.99
11.00	.9929	1.62	17.50	.9492	13.02	24.00	.9091	25.48
11.25	.9912	2.04	17.75	.9475	13.49	24.25	.9076	24.97
11.50	.9894	2.46	18.00	.9459	13.96	24.50	.9061	26.46
11.75	.9876	2.88	18.25	.9444	14.43	24.75	.9047	26.95
12.00	.9859	3.30	18.50	.9428	14.90	25.00	.9032	27.44
12.25	.9842	3.73	18.75	.9412	15.37	25.25	.9018	27.93
12.50	.9825	4.16	19.00	.9396	15.84	25.50	.9003	28.42
12.75	.9807	4.59	19.25	.9380	16.32	25.75	.8989	28.91
13.00	.9790	5.02	19.50	.9365	16.80	26.00	.8974	29.40
13.25	.9773	5.45	19.75	.9349	17.28	26.25	.8960	29.89
13.50	.9756	5.88	20.00	.9333	17.76	26.50	.8946	30.38
13.75	.9739	6.31	20.25	.9318	18.24	26.75	.8931	30.87
14.00	.9722	6.74	20.50	.9302	18.72	27.00	.8917	31.36
14.25	.9705	7.17	20.75	.9287	19.20	27.25	.8903	31.85
14.50	.9689	7.61	21.00	.9272	19.68	27.50	.8889	32.34
14.75	.9672	8.05	21.25	.9256	20.16	27.75	.8875	32.83
15.00	.9655	8.49	21.50	.9241	20.64	28.00	.8861	33.32
15.25	.9639	8.93	21.75	.9226	21.12	28.25	.8847	33.81
15.50	.9622	9.38	22.00	.9211	21.60	28.50	.8833	34.30
15.75	.9605	9.83	22.25	.9195	22.08	28.75	.8819	34.79
16.00	.9589	10.28	22.50	.9180	22.56	29.00	.8805	35.28
16.25	.9573	10.73	22.75	.9165	23.04			

Specific gravity determinations were made at 60°F., compared with water at 60°F.

From the specific gravities the corresponding degrees Baume were calculated by the following formula: Baumé = (140/sp. gr.) – 130.

Baume hydrometers for use with this table must be graduated by the above formula, which formula should always be printed on the scale.

Atomic weights from F. W. Clarke's table of 1901. O = 16.

[27] Authority—W. C. Ferguson. This table has been approved and adopted as a Standard by the Manufacturing Chemists' Association of the United States, and is reproduced by courtesy of the Manufacturing Chemists' Association of the United States.

should be noted that the more concentrated the solution the lower its specific gravity. The Baumé scale given in this case is that of the U. S. Bureau of Standards for light liquids.

ALLOWANCE FOR TEMPERATURE

The coefficient of expansion for ammonia solutions, varying with the temperature, correction must be applied according to the following table:

	Corrections to be added for each degree below 60°F.		Corrections to be subtracted for each degree above 60°F.			
Bé	40°F.	50°F.	70°F.	80°F.	90°F.	100°F.
14	0.015° Bé	0.017° Bé	0.020° Bé	0.022° Bé	0.024° Bé	0.026° Bé
16	0.021 "	0.023 "	0.026 "	0.028 "	0.030 "	0.032 "
18	0.027 "	0.029 "	0.031 "	0.033 "	0.035 "	0.037 "
20	0.033 "	0.036 "	0.037 "	0.038 "	0.040 "	0.042 "
22	0.039 "	0.042 "	0.043 "	0.045 "	0.047 "	
26	0.053 "	0.057 "	0.057 "	0.059 "		

TABLE IX-13

EQUIVALENT FACTORS OF VARIOUS ALKALIES

1 part of:		equivalent to:
NaOH	1.4 parts	KOH
	1.325 "	Na_2CO_3
	1.725 "	K_2CO_3
	0.425 "	NH_3
	3.63 "	triethanolamine
KOH	0.714 parts	NaOH
	0.947 "	Na_2CO_3
	1.233 "	K_2CO_3
	0.302 "	NH_3
	2.59 "	triethanolamine
Na_2CO_3	0.754 parts	NaOH
	1.057 "	KOH
	1.305 "	K_2CO_3
	0.321 "	NH_3
	2.73 "	triethanolamine
K_2CO_3	0.578 parts	NaOH
	0.810 "	KOH
	0.767 "	Na_2CO_3
	0.246 "	NH_3
	2.10 "	triethanolamine
NH_3	2.35 parts	NaOH
	3.29 "	KOH
	3.11 "	Na_2CO_3
	4.06 "	K_2CO_3
	8.53 "	triethanolamine
Triethanolamine	0.276 parts	NaOH
	0.387 "	KOH
	0.365 "	Na_2CO_3
	0.476 "	K_2CO_3
	0.117 "	NH_3

BLEACHING AGENTS FOR SOAP

In this chapter we will deal only with those bleaching agents that serve to bleach soap. Agents for bleaching fats and oils are dealt with under oil and fat refining (Chapter XIII). However, some of the bleaching agents for soap may be used as well for bleaching oils and fats. Since these bleaching agents are all inorganic materials (except for the organic peroxy compound), they will be dealt with before we describe organic soap builders.

(1) Chlorine Compounds

These strong oxidizing compounds containing "active chlorine" comprise the main group of soap bleaching agents. All are produced by the action of chlorine gas (produced by electrolysis of sodium chloride; see Chapter VIII, 1), then thoroughly dried, freed of impurities, and finally liquefied by compression and refrigeration.

Liquid chlorine in steel containers is often used in large soap plants to produce the necessary alkaline bleaching solutions on the spot. The methods of preparation, mainly of *sodium hypochlorite solutions,* are described later.

(A) Chlorinated Lime

Chlorinated lime is used not for bleaching soaps but as a starting point for the preparation of suitable alkaline bleaching liquors. This is especially the case where chlorine is unavailable and when the transportation costs would make the use of prepared sodium hypochlorite solutions too expensive. Chlorinated lime (bleaching powder) is the most suitable and least expensive starting material.

Chlorinated lime is usually prepared by saturating a fine powder of hy-

drated lime $Ca(OH)_2$ in a rotating steel cylinder fitted with blades to facilitate mixing with chlorine at about $50°C$. The reaction occurs according to the following equation:

$$Ca(OH)_2 + Cl_2 \rightarrow Ca\underset{OCl}{\overset{Cl}{<}} \cdot H_2O$$
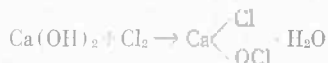
High-grade chlorinated lime (bleaching powder) has the approximate chemical formula $CaCl(ClO) \cdot H_2O$. It is a white hygroscopic powder with a strong odor of chlorine and is stable only when dry and when stored in a cool place in closed container. It is usually marketed in drums (100, 224, 333, 600, and 850 lbs.) or in tins (25 lbs.). The available chlorine in the commercial products varies from 35–70%.

(B) Sodium (or Potassium) Hypochlorite Solutions

Alkali hypochlorite solutions with 7–8% available active chlorine may be prepared from calcium hypochlorite powder and sodium carbonate solution.

100 parts bleaching powder is slurried with 300 parts cold water. Then a solution of 60 parts sodium carbonate (or 75 parts potassium carbonate) in 150 parts warm water are added to the slurry and stirred for about one hour. The mass is allowed to settle overnight and the clear bleaching liquor is drawn off; the residual slurry is washed with water containing some additional Na_2CO_3 (or K_2CO_3). This wash water, after settling, is used again for the preparation of a new bleaching liquor. If calcium hypochlorite is used instead of bleaching powder the alkali carbonates and the amount of water is suitably doubled to obtain the same concentration.

Sodium hypochlorite (soda bleach liquor) is also manufactured directly by the reaction of gaseous or liquid chlorine with caustic soda in a well cooled aqueous solution. There are two general classifications for soda bleach: first, those which contain 3–5% available chlorine for use as a germicide and general oxidizing agent, and, second, those containing 10–15% available chlorine by weight for use as a bleaching agent in the textile industry and laundries, and for other chemical purposes. These stronger solutions are nearly always diluted to lower strengths before being used. They are prepared at high concentrations in order to decrease the bulk for storage and transportation. The reaction takes place acording to the equation:

$$2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$$

Excess alkali is required to stabilize the hypochlorite. In some cases it is desirable to prepare sodium hypochlorite by chlorinating water solutions of sodium hydroxide to which a definite quantity of soda ash has been added.

The presence of iron compounds in sodium hypochlorite solutions causes decomposition. For this reason, the caustic soda solutions must be carefully settled and sometimes filtered before chlorination to remove any iron which

may be present. Proper preparation and cooling of the caustic solutions are important in the manufacture of sodium hypochlorites, and adequate tanks and piping systems must be provided.

The actual chlorination is carried out in nonmetallic tanks, such as specially lined concrete, ceramic vessels, or rubber-lined steel tanks, to prevent contamination from metals. Extra-heavy glass tubing is preferred for conducting chlorine into the solution, although other materials have been used with satisfactory results, depending on operating conditions. Lead tubing may be used for solutions not exceeding about 70 g. per liter of available chlorine without encountering serious difficulties. For satisfactory operation, chlorine should be introduced at least four feet below the surface of the caustic soda solution.

The chlorine control valve should be located as close as possible to the chlorinating tank. Iron pipe or heavy copper tubing of 500 lbs. test pressure per sq. in. may be used for transferring chlorine from the container to the control valve. A special copper tube with clamp and adaptor connections is recommended for joining the valve of the container to the permanent piping. The pressure in the system should be controlled by a chlorine pressure gage of the diaphragm type in the line between the container and the control valve. This is an indispensable item, and is in the same class as a good platform scale, vacuum relief device, and chlorine piping erected in accordance with good high pressure piping standards of workmanship. No plant can handle chlorine safely and intelligently without these.

Since decomposition increases with higher temperatures during chlorination, it is essential that the solution temperature not exceed 85°F. (29.5 C.). In order not to exceed this temperature, mechanical refrigeration is necessary to prepare the stronger solutions and the low temperature can best be maintained during chlorination by circulating a cold brine solution through stoneware coils immersed in the solution. When ice is used to cool the soluton, allowance for it must be made in determining the total quantity of water needed in the chlorination tank. To avoid contamination and subsequent decomposition, the solutions should be handled in stoneware, concrete, rubber-lined, or enameled equipment. Sodium hypochlorite should be stored in a cool dark place, since light and heat accelerate decomposition.

Tests for available chlorine and free alkali in sodium hypochlorite may be made as described under tests for bleach liquor in Part J, Volume II.[28]

Potassium hypochlorite is much less important. It is only used for bleaching "fig soft soaps"; other soft soaps may be bleached with the sodium bleach liquor. The method of manufacture is the same as for sodium bleach liquor, KOH being substituted for NaOH. Detailed information regarding the

[28] See also bulletin on chlorine, Pennsylvania Salt Manufacturing Co., Philadelphia, Pa.

amount of hypochlorite solution for soap bleaching will be given in the chapter on bleaching of soaps (see Chapter XVIII, 1, E).

It must be pointed out that products of the hypochlorite type are not soap builders, and the use of chlorine compounds in washing compounds sold to the public is to be avoided. If hypochlorites are used in laundries, this should be done by experts under controlled conditions.

(2) Peroxide and Similar Compounds

The chief representative of this group is hydrogen peroxide (H_2O_2). It is obtained by the action of acids either on peroxides as Na_2O_2 (sodium peroxide) or BaO_2 (barium peroxide), or on persulfates e.g., $K_2S_2O_8$, produced by anodic oxidation of potassium bisulfate ($KHSO_4$).

Concentrated solutions of H_2O_2 are obtained by concentrating dilute solution under high vacuum. Table X-1, by Slater, [29] gives the specific gravity of solutions in the range of general industrial use.

TABLE X-1

H_2O_2, g./100 g.	Specific gravity	Popular descriptions
3.01	1.009	10 vol.
5.95	1.020	20 vol.
27.52	1.032	100 vol. or 30% by vol.
35.32	1.1365	40% by vol.

The higher concentrations of H_2O_2 are rather stable in contrast to very weak solutions (less than 3% by weight). The pure nearly 100% H_2O_2 is seldom used in the soap industry. Hydrogen peroxide is more often used to bleach the fat stock rather than for bleaching soap. The same applies to an organic peroxide compound: benzoyl peroxide $(C_6H_5CO)_2 \cdot O_2$, an oil-soluble, white, crystalline powder with a melting point of 105°C.

Potassium persulfate ($K_2S_2O_8$), with a molecular weight of 270.31, is a colorless, crystalline powder. It decomposes below 100°C. and is only slightly soluble in water. 3-8 parts of $K_2S_2O_8$ are usually enough to bleach 1000 parts of soap.

Zinc persulfate (ZnS_2O_8) is recommended for bleaching of soap, but is very seldom used for this purpose.

Sodium perborate has already been described in Chapter IX as a special soap builder. It is practically never used as a bleaching agent for the soap itself. The same applies to *sodium percarbonate* and *sodium pyrophosphate perhydrate*, also described in Chapter IX.

[29] V. W. Slater, "Hydrogen Peroxide and Related Compounds in Industry," *Chemistry and Industry*, Feb. 10, 1945.

(3) Reducing Agents

A reducing agent which finds wide application for soap bleaching is *sodium hyposulfite* ($Na_2S_2O_4 \cdot 2H_2O$). Two methods of production are used: one uses zinc dust and sodium bisulfite solution at ordinary temperature; the other consists of treating a suspension of zinc dust suspended in dilute formaldehyde solution with gaseous sulfur dioxide at about 80°C. After this, the solution is neutralized with sodium carbonate to form the sodium salt of hyposulfurous acid which remains in solution. Zinc carbonate is filtered off. The solution containing the $Na_2S_2O_4$ is salted-out with sodium chloride. The hydrated sodium hyposulfite crystallizes in needles and is in turn filtered off. The crystals are dried *in vacuo* with the aid of alcohol.[30]

The sodium hyposulfite of commerce is a colorless crystalline powder of the formula $Na_2S_2O_4 \cdot 2H_2O$ (mol. wt. 210.15), soluble in water. The dry powder is stable, but it decomposes when it becomes wet or goes into solution. It is marketed in cans (50 lbs.) or drums (120, 125, and 250 lbs.).

For soap bleaching, 1–3 parts per 1000 parts soap are usually sufficient.

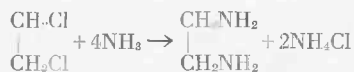[30] L. A. Pratt. "Sodium Hydrosulphite as a Dry Powder," *Chem. & Met. Eng., 31,* 11 (1924).
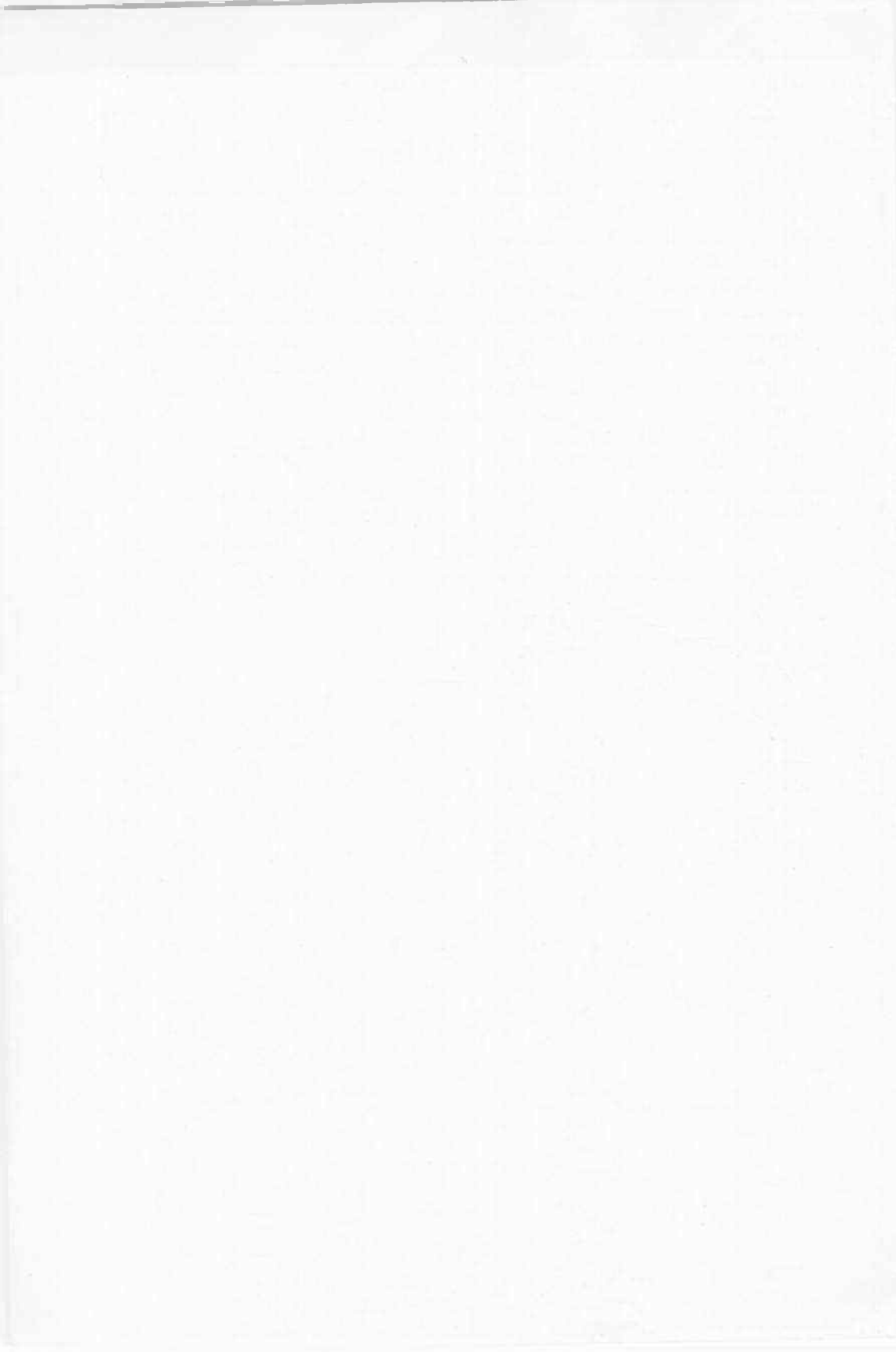
ORGANIC SOAP BUILDERS
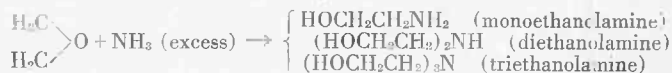
(1) Organic Derivatives of Ammonia

Organic bases may be considered as a special group of soap builders. These organic amines have special qualities as emulsifiers with fatty acid soaps.

The *ethylenediamines* are manufactured by chlorinating ethylene, C_2H_4 (a by-product of, for instance, the petroleum industry) and reacting the product with concentrated ammonia water in an autoclave at 110–150°C.:

$$\begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix} + 4NH_3 \rightarrow \begin{matrix} CH_2NH_2 \\ | \\ CH_2NH_2 \end{matrix} + 2NH_4Cl$$

A large excess of ammonia is necessary in order to favor the formation of the primary amine over the various secondary products, but even when using a surplus of ammonia only 40% yield of primary amine is obtained.[31]

The *ethanolamines*[32] are obtained when ethylene oxide (a gas produced by catalytic oxidation of ethylene) is bubbled through a 28% ammonia solution at 50–60°C., according to the following equation:

$$\begin{matrix} H_2C \\ \quad \\ H_2C \end{matrix} \!\!\!>\!\! O + NH_3 \text{ (excess)} \rightarrow \left\{ \begin{matrix} HOCH_2CH_2NH_2 & \text{(monoethanolamine)} \\ (HOCH_2CH_2)_2NH & \text{(diethanolamine)} \\ (HOCH_2CH_2)_3N & \text{(triethanolamine)} \end{matrix} \right.$$
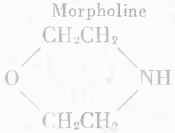
Triethanolamine saponifies about twice its weight of stearic or oleic acids. Generally, it must be emphasized that *all* organic amine bases saponify only fatty acids and not neutral fats and oils.

[31] E. E. Curme, U. S. Pat. 1,832,534 (1931), described in P. H. Groggins, *Unit Processes in Organic Synthesis*, 2nd ed. McGraw-Hill, New York, 1938, pp. 342, 343.

[32] R. N. Shreve, *The Chemical Process Industries.* McGraw-Hill, New York, 1945, p. 911.

In Table XI-1 some of these amines are tabulated with their physical and chemical properties. Triethanolamine is mainly used in the soap industry, especially for the preparation of shaving creams, shampoos, liquid soaps, dry cleaning and solvent soaps, and special cleaners, etc.

TABLE XI-1*

	Morpholine	Monoethanolamine	Diethanolamine	Triethanolamine
Formula	$O\diagup\genfrac{}{}{0pt}{}{CH_2CH_2}{CH_2CH_2}\diagdown NH$	$HOCH_2CH_2NH_2$	$(HOCH_2CH_2)_2NH$	$(HOCH_2CH_2)_3N$
Mol. wt. (theor.)	87.12	61.08	105.94	149.19
Equiv. wt.	Mol. wt.	Mol. wt.	Mol. wt.	Mol. wt.
Sp.gr., 20/20°C.	1.0017	1.0179	1.0920 at 30/20°	1.1258
Blg. range, °C./760 mm.	120–132	160–176	B.p. 269.1	B.p. 208 (10 mm.)
pH, 25% soln., 25°C.	11.4	12.1	11.5	11.2

* Courtesy Carbide and Carbon Chemicals Corporation.

The Board of Standards of the Toilet Goods Association, T.G.A. Specification No. 18, defines triethanolamine as a mixture of alkanolamines consisting chiefly of triethanolamine, with variable amounts of monoethanolamine and diethanolamine. It should meet the following standards:

Color—Must meet buyer's specifications when tested by prescribed method.
Odor—Not more than slightly ammoniacal.
Solubility—Soluble in chloroform. Miscible in all proportions with alcohol and water.
Specific gravity—1.1204 to 1.1284 at 25/25°C.
Refractive index—1.4800 to 1.4850 at 20°C.
Equivalent weight—140–145.
Ash—0.03% maximum.
Lead—1 part per million maximum, as Pb.
Arsenic—1 part per million maximum, as As_2O_3.
Substances reacting with periodate—Not more than 6.2 ml. of 0.1 N iodine is required per 0.1 g. of the sample used in the test.

Another organic amine base is *cyclohexylamine* ($C_6H_{11}NH_2$). The pure compound has the following properties:

Boiling point at 750 mm.	134.5°C.
Crystallizing point	−17.7°C
Specific gravity at 25°C.	0.8647
Molecular weight	99

The technical grade, as produced in the United States, has the following specifications:

Specific gravity at 15.5/15.5°C.	0.870–0.874
Distillation range, first drop	132.0°C.
Min. 95%	up to 136.0°C.
Dry point	137.5°C.

Cyclohexylamine is a stronger base than ammonia and the ethanolamines, and forms stable salts. Being a powerful base, it decomposes most esters. It is volatile in steam, forming an azeotropic mixture containing 44% amine, and boiling at 96.4°C. It can be extracted from aqueous solutions by hydrocarbons.

Cyclohexylamine attacks copper, copper alloys, lead, and zinc in the cold; when hot, it attacks nickel and, very slowly, aluminum. It has no action on iron or stainless steel. It exhibits a strong solvent action, and with fatty acids forms salts which are powerful emulsifying agents. Since the base is soluble in water, the emulsifying agent can be formed *in situ* during the intimate mixing of the ingredients.

Cyclohexylamine fatty acid soaps may form the basis for special textile and dry cleaning soaps and for the manufacture of soap containing agricultural emulsions and special cleaners.[33]

With aminoethylethanolamine, a cyclic compound is formed which, besides being a synthetic emulsifying agent, is also cationic. Additional amine-type products commercially available for neutralizing fatty acids to specialty-type soap products or synthetic detergents are: triethylenetetramine; tetraethylenepentamine; 2-amino-2-methyl-1,3-propanediol; 2-aminomethyl-3-hexanol; tri(hydroxymethyl)aminomethane; 2-amino-2-methyl-1-propanol.

A new organic soap builder is now on the market in the United States under the name of Sequestrene (Alrose Chemical Co.). Chemically this material is ethylenediamine tetraacetic acid. This compound forms salts with sodium or potassium by partly or completely neutralizing the acetic acid groups in the molecule. The completely neutralized type is the most suitable for use in soaps and detergents. Such additions, about 1.5 to 3%, reduce to a minimum the lime and magnesium sensitivity of soap. Calcium and magnesium ions and, *e.g.*, iron ions as well, are "sequestered" by complex formations and thus rendered harmless. In addition, the potassium salts of ethylenediamine tetraacetic acid serve as efficient clarification agents for liquid soaps. This type of organic soap builder and sequestering agent was first developed in Germany by the I. G. Farben under the trade name Trilon.

(2) Organic Derivatives of Cellulose, etc. as Soap Builders and Fillers
(A) STARCH

Starch, like sugar, is a carbohydrate and occurs as such in plants. Corn is 65% starch; all other kinds of grains contain a high percentage of starch. The raw potato contains 15% starch or about 75% on a water-free basis. Starch is extracted with water from the pulped material, from which it deposits in a short time as a white powder. This is filtered off and dried.

Since starch occurs in abundance in nature, and since it is a relative cheap technical product which swells to form a transparent gel, it was used at an

[33] *Manufacturing Chemist*, 17, 154 (1946).

early date as a filler in soap, especially in times of fat and oil scarcity. Radley[34] quotes the following opinions about the use of starch in soaps mainly from German sources:

"The use of starch in soap is stated by some workers to be detrimental, especially if the soap is to be used to wash fabrics printed or dyed with vat colours, on the ground that these colours are reduced by the combined action of the starch and its by-products in the presence of the alkali. Such an action would render the dye-stuff soluble and therefore loose to washing."

On the other hand, some workers prefer the use of starch to that of sodium silicate. Kröner and Steinhoff[35] have shown that on heating starch for periods varying from 0.5 to 12 hours in the presence of a 2% soap solution, alone, with sodium silicate, or with soda lye, no measurable amounts of reducing substances were formed which could be detected by Ost's tests or by Fehling solution. Despite the elaborate tests performed by these authors, further work on a large scale is needed before the matter can be settled, but the balance of evidence suggests that the inclusion of starch is practically harmless, and that it offers certain advantages which will not be overlooked by the trade.

For toilet and milled soaps the starch is added in powder form to the chips before milling. If desired, it can be used in the manufacture of soap flakes, but its use in soap powders is uneconomical, with the exception of shaving powders. The following example illustrates the composition (in parts) of such a shaving powder:

Castile soap powder	800
Maize starch	200
Cassia oil	6
Caraway oil	1
Geranium oil	3

The powders are first mixed, the oils are added, and the whole remixed.

It is interesting that an attempt was made to use a modified starch product as a detergent practically without soap, according to A. L. Sodergreen (U. S. Pat. 2,049,476) by heating corn flour to 120°C. or lower in the presence of moisture to break down the protein matter and to hydrolyze the starch. The mixture is then made alkaline with caustic soda and reheated under pressure to saponify the oil present, any excess caustic soda being neutralized finally with carbon dioxide under pressure.

(B) METHYL- AND ETHYLCELLULOSE

These products, produced by the methylation or ethylation of cellulose, were introduced as a soap-filling material in Germany in 1935 under the trade name of Tylose, and marketed in the United States some time later.[36]

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[34] J. A. Radley, *Starch and Its Derivatives*, 2nd ed., p. 349. London, Chapman & Hall, 1943; Van Nostrand, New York, 1944.

[35] W. Kröner and G. Steinhoff, *Seifensieder Ztg.*, 63, 272 (1938).

[36] *Revue des Produits chimiques*, 42, 193–198, 225–258 (1939); through *Soap*, 15, 57–8 (July, 1939).

Now, there are on the market in the United States many brands of methyl- and ethylcellulose under different trade names; some of the brands are quite suitable as additions to soap. Usually methylcellulose is sold in the form of white flakes or powder which may be dissolved in cold water to form viscous solutions that can be added to liquid or soft soaps. Most types of ethylcellu- loses are water insoluble. However, some types are water soluble and only these are suitable as soap fillers.

Methylcellulose is a valuable soap aid, since it lowers the surface tension of water and helps create a more persistent and copious lather. It possesses some detergent power of its own and thus permits it to decrease the amount of fatty acids present without lowering the quality of the soap. It is claimed to aid the keeping quality of soap and prevents efflorescence. In the manufacture of milled soap, addition of methylcellulose increases plasticity so that toilet soaps, shaving soaps, etc. are easier to work up.

To prepare an alkaline methylcellulose solution for use in soap, add 4 kg. of caustic potash or caustic soda, 40° Bé to 40 kg. of boiling water, stir and add 4 kg. of methylcellulose powder. Mix well and let stand for a half hour, then add with stirring 52 kg. of cold water. Mix again the next day, when a smoth mucilaginous product is obtained. This gives a very unctuous soap when caustic potash is used in its preparation.

A suitable addition to paste soap is to add, for each 100 kg. of soap a mix- ture of 20 kg. of sodium silicate (36–38° Bé), 3 kg. of caustic soda (40° Bé), and 3 kg. of water, all brought to a temperature of 70–80°C., after which 6 kg. of a cold solution of methylcellulose is added little by little. By this means a hard soap with a fatty acid content of 48% can be obtained.

A transparent soft soap is prepared as follows: 1000 kg. of oil or fatty acid is saponified with caustic potash and the necessary potash added, giving 2200 kg. of soap base. To this add 150 kg. of potassium hypochlorite (10° Bé), 150 kg. of a solution of potassium chloride (10–20° Bé), 100 kg. of sodium silicate (36° Bé), 350 kg. of methylcellulose solution, and 50 kg. of caustic potash (40° Bé). This soap becomes transparent after 2–3 days.

To prepare a concentrated solution, the flakes are allowed to stand in water for several hours, or preferably overnight, when they first swell and then dissolve. Solutions of methylcellulose are neutral, with a pH value of 7.5, and are stable to alkali and to fairly concentrated acid. Methyl- as well as ethylcellulose is also used in sizing pastes containing soaps for application in textile printing and finishing.

(C) SODIUM CARBOXYMETHYLCELLULOSE (CMC)

A portion of the complex molecule representing this material is given in Fig. XI-1.[37] During World War II, the compound was widely used in

[37] T. H. Vaughn and H. E. Tremain, *Soap & Sanit. Chem.*, 24, No. 3, 38 (1948).

Germany as a soap extender (Tylose HBR). CMC is produced by reacting cellulose with caustic soda and condensing the reaction product with chloro-acetic acid. Tests performed after the war in the United States have confirmed the detergency efficiency of the compound, which had been used previously in ice cream manufacture, in paper sizing, and in other applications, and was therefore available commercially (CMC or Na-CMC). The compound is used in laundering, particularly in combination with synthetic detergents,[38] since it has the unique property of increasing the suspending power of soil in the detergent solution—a particular deficiency in the alkyl-aryl-type synthetic detergent and more or less common to them all. Soap, on the other hand, is not deficient in this respect, so that CMC has less importance as a building material for soap. But even in soap, especially "built up" soap powders, additions of about 5% CMC generally promotes soil

Fig. XI-1. Diagram of a portion of a molecule of sodium CMC showing four of the basic units of which the molecule is composed.[37]

removal and whiteness retention.[39] Dutch research on CMC has been published[39a] and demonstrates the efficiency of CMC as a soap builder in percentages up to 10%.

(D) Lignin

Lignin occurs in nature in woody material, where it appears to be associated with the encrusting substances in which cellulose fibers are imbedded. The waste quantities of lignin available in one or the other form as a by-product of any process involving the separation of cellulose from noncellulosic materials in wood, etc. has made it imperative to search for any use of lignin in industry.[40] Especially in times of fat scarcity, the attention of soap experts is focussed on this large source of a potential soap builder. During the process of separation of cellulose from noncellulosic material, lignin by the sulfite process will be found in the waste liquor of this process. Since sulfite waste liquor is a source of lignin which is fairly abundant in the United States,

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[38] T. H. Vaughn and C. E. Smith, *J. Am. Oil. Chem. Soc.*, 25, 44 (1948).

[39] *Carbose for Detergency Promotion*, Wyandotte Chemicals Corporation (1950); F. J. Pollak, *Soap, Perfumery and Cosmetics*, 24, 991–995 (1951).

[39a] K. J. Nieuwenhuys, *Soap, Perfumery and Cosmetics*, 23, 1229 (1950).

any use for this material is welcomed because most of it is discarded into rivers and streams, where it constitutes a pollution problem. The lignin in sulfite waste liquor is in the form of lignosulfonic acid, and has associated with it sulfites and sulfates as well as the usual degradation products of wood.[41]

Braun[42] gives some pertinent information about the use of sulfite waste liquor as a constituent of soap. He points out that the very dark color of crude sulfite waste liquor makes it impossible to use it as a soap or detergent ingredient, but a specially refined sulfite waste liquor may be used to produce, e.g., a soft soap with only 10% fatty acids and 60% refined sulfite waste liquor. It is also possible, according to Braun, to produce a common household soap from 100 parts curd soap (with about 63% fatty acids) with 25 parts refined sulfite waste liquor. He mentions the textile auxiliaries *Dekol* and *Protectol* (of I. G. Farbenindustrie A.-G.) which were sodium lignosulfonates. Braun also points out that detergents from sulfite waste liquor have a cleansing effect even in sea water and have lime-dispersing power in hard water.

However, even refined products from sulfite waste liquor which were on the market in Germany (e.g., *Zewa* powder) became yellow-brown liquids if diluted with water. Still, their detergent effect was not bad and soap products containing refined concentrated sulfite waste liquor in powder form could be produced.[43]

The following formulas for a washing powder are typical:

1. 20 parts pure powdered soap.
   40 parts powdered sulfite liquor.
   40 parts soda ash.
2. 20 parts pure powdered soap.
   40 parts powdered sulfite liquor.
   30 parts soda ash.
   10 parts sodium perborate.

Even soap flakes with 10–30% or toilet soap with 10% powdered sulfite liquor were produced by adding the powdered sulfite liquor during the milling process.

E. Schubert and H. Pierer (U. S. Pat. 2,352,021) describe the manufacture of detergents of improved properties containing 20 to 50% of *alkali lignin,* which is used here to designate the water-soluble reaction product of lignin and an alkali.

Keilen[40] points out that the term "alkali lignin" as used in the patent is in conflict

[40] H. F. Lewis, *Chem. Eng. News, 23,* 1074–1080 (1945) (a general account of the use of lignin). J. J. Keilen, *Soap, 21,* No. 3, 40–41, 146 (1945) (lignin as a detergent ingredient).

[41] J. P. Casey, *Pulp and Paper,* Vols. I–II. Interscience, New York, 1952.

[42] K. Braun, *Seifensieder Ztg., 64,* 207–208 (1937).

[43] R. Krings, *Seifensieder Ztg., 64,* 337–338 (1937).

with the commonly accepted terminology in the United States, since it is generally used to designate a product resulting from an alkaline digestion of vegetable matter which may still contain the alkali, or which may have been converted to a completely organic material by treatment with acid. Such confused terminology has long been a problem to chemists and other technologists attempting to find commercial uses for this potentially abundant material.

The following formula for a washing agent is suggested:

20 parts of an alkyl or aryl ester of sulfuric acid and higher molecular fatty acids.
15 parts sodium carbonate.
 8 parts sodium perborate.
24 parts alkali lignin.
 4 parts water glass.
14 parts sodium sulfate.
15 parts water.

Lignin can also be used advantageously with any soap to increase the efficiency in hard water. This may be due to the protective colloid action of the lignin, to the formation of calcium salts of the lignin itself, or to the adsorptive power of the lignin for the calcium. All three properties have been attributed to lignin.

Keilen draws attention to another source of lignin besides sulfite waste liquor and wood saccharification residues. This is from the waste liquors of the soda or sulfate process for wood pulping. At the present time these liquors are burned in order to recover the sodium compounds for reuse in pulping. The precipitation of the lignin by means of acid still permits the recovery of a large percentage of the sodium compounds, and interferes but slightly with normal mill operation. It is estimated that in 1943 there was potentially available over a million tons of lignin from the soda and sulfate pulping processes.

Moreover, the lignin from this source is readily purified, so that it may be made available virtually free of inorganic contamination, and with a minimum of organic impurities. Such lignins would require only the addition of caustic to be ready for use by the soap manufacturer. It is quite likely that with lignin chemistry making rapid strides a lignin derivative might be found to be as effective a detergent and soap builder as CMC and possible much cheaper. This is the reason for going into details about the use of lignin in soaps even if at the present time lignin seems to be seldom used in soap and soap products.

(E) FLUORESCENT DYES

Within the past four or five years the use of fluorescent or "optical" dyes has become so widespread in the manufacture of soap and synthetic detergent powders that in the United States, at least, it is very difficult to find a product of this type that does not use them. In practice, the dye is added to the extent of about one pound of the dye to 1000 to 3000 pounds of the soap in the crutcher or kettle. The dye is absorbed by the cloth in washing. In sunlight,

a portion of the invisible ultraviolet light falling on the fabric is converted into visible blue light, so that the reflected light is actually increased by the presence of the dye. This masks the yellowing of the cloth, as does ordinary blueing, only in a different and more effective way, and makes the fabric appear "whiter than new." Dyes of this type are now available in a number of types and strengths from all large dye manufacturers in all parts of the world. A discussion of the development and chemical nature of the dyes is beyond the scope of this book. However, a few points in this regard will help the soap boiler in understanding the problem of their use.

Fluorescent dyes differ widely in structure. They also differ in their ability to absorb on fabric, to withstand decomposition under light, and to withstand such bleaching agents as chlorine. Each dye is a compromise of these many desirable characteristics. A dye that is unstable to light, for example, not only can cause a wash to look less bright, but it may even give it an off-yellow shade. Generally speaking, however, the results are good and when used with discretion the dyes can be a very useful adjunct to the product. Especially in soap and detergent powders the addition of from 0.05–0.1% "optical bleach" on the weight of the powder is to be recommended. There seems to have been more readiness to use these new compounds with cellulosic fabrics than with wool or silk. This is partly because the earlier products marketed for use in the textile industry were designed especially for use on cellulosic materials and partly because a "warmer or creamier" tint is associated with wool. The fluorescent compounds recommended for cotton and other cellulosic materials are similar in chemical structure to the direct dyes with the exception that the chromophore, i.e., color-producing constituents, are absent in the molecules. They are therefore, in effect, colorless direct dyes and behave as such.[44]

(I) (II)
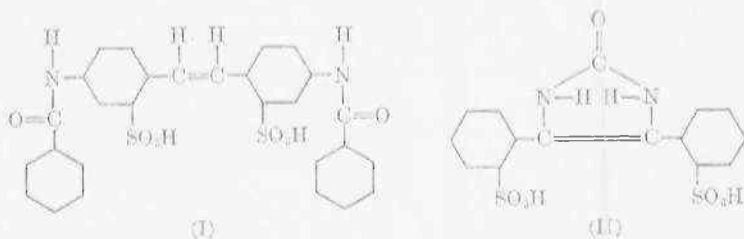
It must not be assumed that the optical bleaching agents are a substitute for ordinary bleaching in laundry operation, or for that matter, in textile processing, for they have no such properties of their own in the normal sense that a bleaching agent has. They can be used with success only to create, in fact, an entirely new standard of whiteness on goods which have been washed and/or bleached by ordinary methods, or to make the color of a mild bleach

[44] C. R. Tritman, *Textile J. Australia*, 26, 1224–27 (1952).

comparable with that of a stronger one. A further important point is that the whiteness produced by optical bleaching agents is not permanently fast to light and after prolonged exposure to sun rays the original shade of the cloth will reappear.

Some typical compounds used as optical bleach are[45] derivatives of coumarin, diaminostilbene, 4,4′-bis-(benzamidol)-2.2′-stilbenedisulfonic acid (I), benzimidazole, benzidine, diaminophenylures, diaminobenzyl, diphenylimidazolone (II), phenylbenzethiazole, benzocoumarin, and tris(aminophenyl)-ethylene.

[45] E. I. Stearns, T. F. Cooke, and H. E. Millson, *Soap & Sanit. Chem.*, *26*, No. 3 (1950).

PART B (continued)

RAW MATERIALS OF SOAP MANUFACTURE

The Fatty Raw Materials
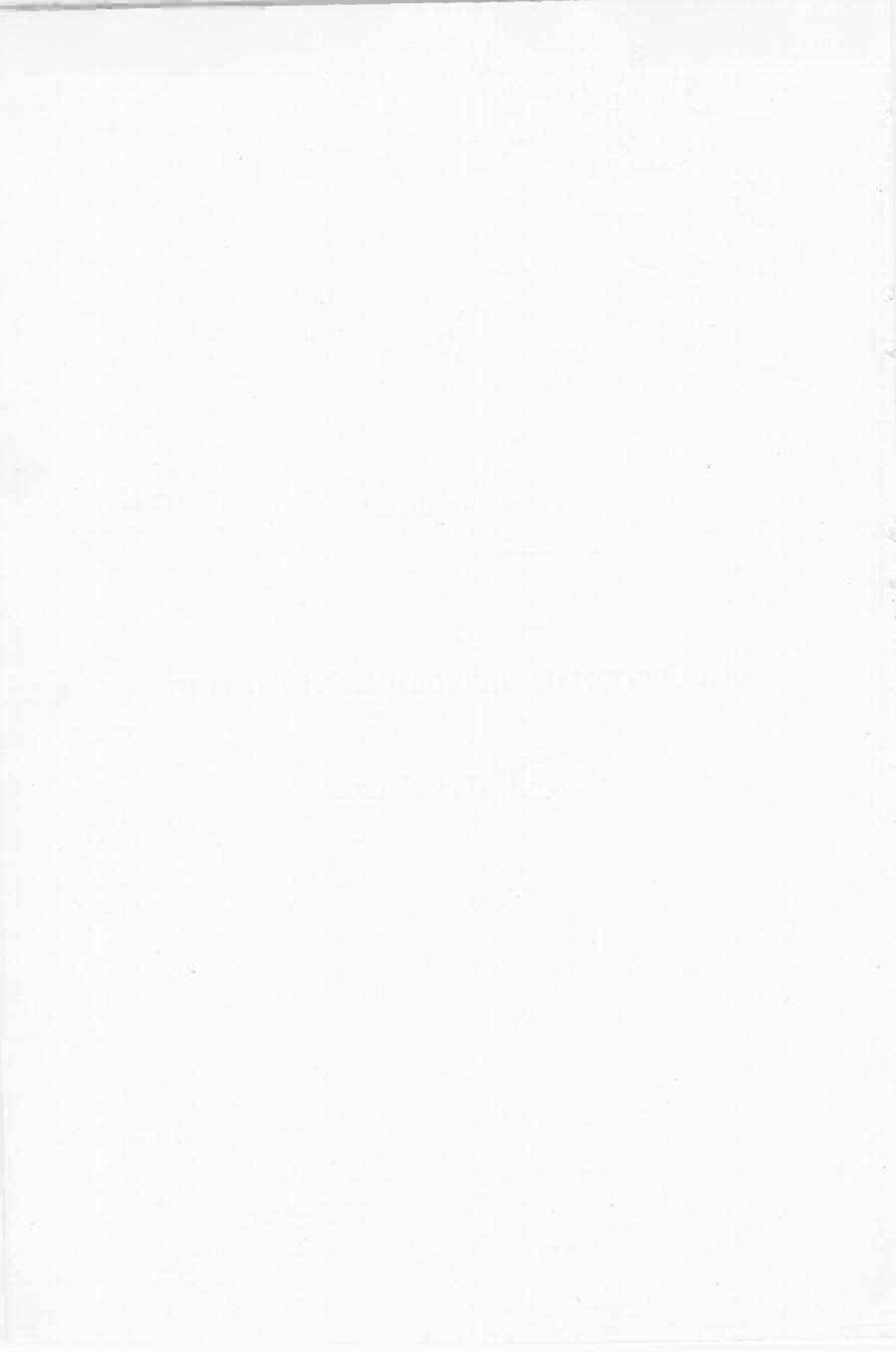
INTRODUCTION

(1) General Definitions and Properties of Oils and Fats

Before discussing the chemical and technological aspects of oil and fat production, a glance at Table XII-1 will give an idea of the extent of the consumption of animal and vegetable fats in the American soap industry. From this table, not only the amount of oils and fats can be seen, but also which oils and fats are preferably used in the soap industry.

A *fat* or an *oil* is a substance which is lighter than water (specific gravity between 0.910–0.970). It is insoluble in water; it leaves a "fat stain" on paper. Fats and oils, with the exception of castor oil—which has an hydroxyl group in the carbon chain—are sparingly soluble in ethyl alcohol. However, fatty acids are soluble in alcohol, so that with the increase of free fatty acid content of a fat or oil, solubility in alcohol increases. All fats and oils, except castor oil, are soluble in such solvents as ether, chloroform, carbon tetrachloride, carbon disulfide, benzene, and petroleum ether. Castor oil is an exception, since it is only sparingly soluble in petroleum ether.

Oils and fats are relatively stable natural compounds. Decomposition is well advanced at temperatures higher than 200°C. In fact, it probably starts well below 200°C., depending largely on the type of oil or fat under consideration.

Mineral oils also belong to the class of oils, but have a completely different chemical composition than the natural saponifiable fats which are derived from the animal or vegetable world. Only the latter fats and oils are soap forming and only these shall be dealt with in this chapter. (Soft paraffin wax, a product of the petroleum industry, will be dealt with in the chapter on toilet soap manufacture, where it serves as a superfatting agent.)
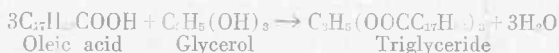
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Chemically speaking, fats and oils belong to the class of esters. Organic esters are compounds of acids with alcohols. In the case of natural oils and fats the acids are higher fatty acids with glycerol, a tribasic alcohol, as its base. This means that one molecule of glycerol combines with three molecules of fatty acids to form a neutral triglyceride. If one molecule of glycerol

TABLE XII-1

FACTORY CONSUMPTION OF ANIMAL AND VEGETABLE FATS
AND OILS IN THE MANUFACTURE OF SOAP
Source: U. S. Department of Commerce Bureau of the Census
(Quantities in thousands of pounds)

	1945	1946	1947	1948	1949	1950
Cotton oil	1,695	522	920	720	—	—
Peanut oil	846	7,347	374	271	—	—
Coconut oil	59,353	184,906	511,313	417,256	282,455	256,973
Corn oil	721	299	446	185	—	—
Soybean oil	4,210	3,545	5,375	2,794	—	—
Olive edible	18	1	4	—	—	—
Olive ined.	302	193	324	469	—	—
Olive foots	1,685	608	440	—	—	—
Palm oil	24,500	7,417	1,091	—	—	—
Palm kernel	29,967	18,939	—	—	—	—
Rapeseed oil	—	16	—	—	—	—
Linseed oil	915	576	276	339	—	—
Perilla oil	—	—	—	—	—	—
Castor oil	1,396	543	1,087	726	—	—
Sesame oil	—	—	—	—	—	—
Babassu oil	32,476	35,834	14,581	—	—	—
Other veg.	2,338	448	557	6,720	16,656	—
Stearin (edible)	—	—	—	—	—	—
Lard	82,070	744	5,973	3,716	—	—
Oleo oil	3,685	3,082	40	—	—	—
Tallow (edib.)	32,067	6,895	7,087	1,562	—	—
Tallow (ined.)	952,334	871,968	1,108,909	980,670	961,505	1,006,833
Grease	411,600	337,871	416,838	470,784	384,092	365,143
Neat's foot	7	41	23	2	—	—
Marine oils	2	4	10	1	—	—
Fish oils	114,344	39,710	42,540	35,476	—	—
Total	2,151,011	1,882,511	2,363,015	2,139,742	1,847,976	1,885,365

is bound to one molecule of fatty acid, two OH groups of the glycerol molecule remain free and a *monoglyceride* is formed; in the case of two molecules of fatty acids bound to one molecule of glycerol, one OH group remains free, and a *diglyceride* is formed. These mono- and diglycerides are sometimes present in minute percentages in natural oils and fats, but as manufactured products are important as emulsifiers. They may be formed synthetically

or during the saponification process in the interim stage of splitting (see Chapters II and XV, 1). The process of esterification of oleic acid with glycerol is given as an example of the chemical formation of a *triglyceride*. (In nature this process of triglyceride formation in the plant or animal body is much more complex and is beyond the scope of this book.)
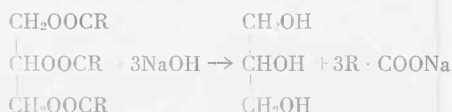
$$3C_{17}H_{33}COOH + C_3H_5(OH)_3 \rightarrow C_3H_5(OOCC_{17}H_{33})_3 + 3H_2O$$

Oleic acid   Glycerol   Triglyceride

or:

$$3R \cdot COOH + C_3H_5(OH)_3 \rightarrow C_3H_5(OOC \cdot R)_3 + 3H_2O$$

(where R is the carbon chain and the COOH group is the characteristic group for a fatty acid.

If a natural fat (triglyceride) is split (Ch. II, 2 and XIII, 1), the reaction occurs in the opposite direction. For the saponification process the following reaction takes place:

$$\begin{matrix} CH_2OOCR & & CH_2OH \\ CHOOCR & + 3NaOH \rightarrow & CHOH & + 3R \cdot COONa \\ CH_2OOCR & & CH_2OH \end{matrix}$$

Fats and oils almost invariably consist of mixed glycerides in which two or even three different fatty acids are present.[1] It is very interesting to note that, among some fifty fatty acids found in nature, almost all are straight-chain acids containing an even number of carbon atoms. This fact was later taken as a basis for an explanation of fat metabolism in the animal and human body. The only odd-numbered fatty acid isolated from fats is iso-valeric acid, $(CH_3)_2CHCH_2COOH$, which occurs in relatively large amounts in the dolphin and porpoise.
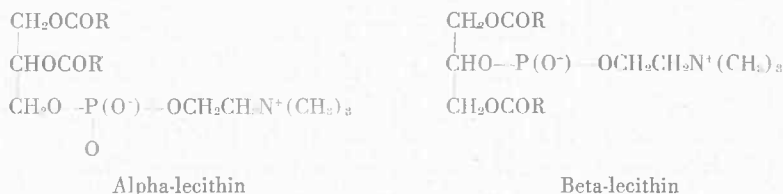
Before dealing with the different fatty acids of which the natural triglycerides are formed, the lesser constituents of fats and oils will be discussed. We can correctly suppose that chemically pure triglycerides would be almost tasteless. The taste and odor of fats and oils is mainly caused by minute quantities of phosphatides, carotenoids, and similar pigments, as well as by

Cholesterol

[1] T. P. Hilditch, *The Chemical Constitution of Natural Fats*, 2nd Ed., Wiley, New York, 1947.

volatile fatty acids, aldehydes, and ketones. Except for color and odor, these substances are unimportant for the soapmaker. However, cholesterol and its derivatives occurring in wool fat products have found entrance into the soap industry, especially for cosmetic and medical soaps.

The structure of the phosphatides, *e.g.*, lecithin, is similar to that of the triglyceride itself. Lecithin has also found use in the soap industry as a special addition to soap. On hydrolysis, lecithins yield two molecules of fatty acids, one molecule of phosphoric acid, and one molecule of choline:

CH₂OCOR   CH₂OCOR

CHOCOR   CHO—P(O⁻)—OCH₂CH₂N⁺(CH₂)₃

CH₂O—P(O⁻)—OCH₂CH₂N⁺(CH₂)₃   CH₂OCOR

        O

    Alpha-lecithin   Beta-lecithin

R denotes the carbon chain of the fatty acids, or more simply:

$$
\text{glycerine}
\begin{cases}
\text{fatty acid radical} \\
\text{fatty acid radical} \\
\text{phosphoric acid + choline radical}
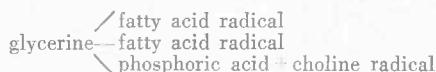\end{cases}
$$

TABLE XII-2

NATURALLY OCCURRING SATURATED FATTY ACIDS[2]

Common name	Systematic name	No. of C atoms	Mol. wt. of acid	Mol. wt. of tri- glyceride	Neutral. value of acid	Sapon. value of triglyceride	M.p. of acid, °C.
Butyric	Butanoic	4	88.10	302.4	636.8	556.6	− 8
Caproic	Hexanoic	6	116.16	386.5	483.0	435.5	− 3.4
Caprylic	Octanoic	8	144.21	470.7	389.0	357.6	16.7
Capric	Decanoic	10	172.26	554.8	325.7	303.4	31.6
Lauric	Dodecanoic	12	200.31	639.0	280.1	263.4	44.2
Myristic	Tetradecanoic	14	228.36	723.1	245.7	232.8	54.4
Palmitic	Hexadecanoic	16	256.42	807.3	218.8	208.5	62.9
Stearic	Octadecanoic	18	284.47	891.5	197.2	188.8	69.6
Arachidic	Eicosanoic	20	312.52	975.6	179.5	172.5	75.4
Behenic	Docosanoic	22	340.57	1059.8	164.7	158.8	80.0
Lignoceric	Tetracosanoic	24	368.62	1143.9	152.2	147.1	84.2
Isovaleric	—	5	102.13	344.4	549.3	488.7	

Tables XII-2 and XII-3 show the properties of different saturated and un-saturated fatty acids occurring in natural fats and oils.[2]

(2) Classification and Composition of Oils and Fats

The nature of an oil or fat depends largely on its fatty acid composition. Oils with a higher amount of unsaturated fatty acid (*i.e.*, one or more double bounds in the molecule) are usually liquid. Fats with a lower amount of

[2] A. E. Bailey, *Industrial Oil and Fat Products*, 2nd ed., Interscience, New York, 1951, pp. 10, 41, 46, 84.

TABLE XII-3

Characteristics of Unsaturated Fatty Acids[2]

Fatty acid	No. of C atoms	No. of double bonds	Mol. wt. of acid	Mol. wt. of triglyceride	Neutr. value of acid	Sapon. value of triglyceride	Iodine value of acid	Iodine value of triglyceride	M.p., °C.
Decenoic	10	1	170.24	548.8	329.6	306.7	149.1	138.77	
Dodecenoic (lauroleic)	12	1	198.29	632.9	282.9	265.9	128.0	120.32	
Tetradecenoic (myristoleic)	14	1	226.34	717.1	247.9	234.7	112.1	106.20	
Hexadecenoic (palmitoleic)	16	1	254.39	801.2	220.5	210.1	99.78	95.04	—
Octadecenoic (oleic, etc.)	18	1	282.44	885.4	198.6	190.1	89.87	86.01	normal (cis) 16.3 (iso) 44–45
Eicosenoic (gadoleic)	20	1	310.50	969.5	180.7	173.6	81.75	78.54	—
Docesenoic (erucic, etc.)	22	1	338.55	1053.7	165.7	159.7	74.98	72.27	—
Tetracosenoic (selacholeic)	24	1	366.60	1137.9	153.0	147.9	69.24	66.93	—
Octadecadienoic (linoleic)	18	2	280.43	879.3	200.0	191.4	181.04	173.21	− 6.5
Hexadecatrienoic	16	3	250.36	789.2	224.1	213.3	304.17	289.48	
Octadecatrienoic (linolenic)	18	3	278.41	873.3	201.5	192.7	273.52	261.61	− 12.8
Octadecatetraenoic	18	4	276.40	867.3	203.0	194.1	367.35	351.21	
Ricinoleic (with one OH group)	18	1	298.44	933.4	188.0	180.3	85.06	81.58	5.5
Eicosatetraenoic (arachidonic, etc.)	20	4	304.45	951.4	184.3	176.9	333.51	320.17	—
Eicosapentaenoic	20	5	302.43	945.3	185.5	178.1	419.67	402.79	—
Docosapentaenoic	22	5	330.49	1029.5	169.8	163.5	384.04	369.85	—
Docosahexaenoic	22	6	328.47	1023.5	170.8	164.4	463.68	446.42	—
Tetracosapentaenoic	24	5	358.54	1113.7	156.5	151.1	353.99	341.89	—
Tetracosahexaenoic	24	6	356.52	1107.6	157.4	152.0	427.20	412.52	—
Hexacosapentaenoic	26	5	386.59	1197.8	145.1	140.5	328.31	317.88	—
Hexacosahexaenoic	26	6	384.57	1191.8	145.9	141.2	396.04	383.38	—

B. RAW MATERIALS

TABLE XII-4[a]

VEGETABLE OILS AND FATS

No.	Composition of fatty acids	Almond oil (nd)	Babassu oil (nd)	Borneo tallow (nd)	Castor oil (nd)	Chinese vegetable tallow (nd)	Cocoabutter (nd)	Coconut oil (nd)	Cohune nut oil (nd)
	(a) Saturated Acids								
1	Caproic, $C_6H_{12}O_2$	—	0.1	—	—		—	Trace	Trace
2	Caprylic, $C_8H_{16}O_2$	—	6.5	—	—		—	8.0	7.5
3	Capric, $C_{10}H_{20}O_2$	—	2.7	—	—		—	7.0	6.5
4	Lauric, $C_{12}H_{24}O_2$	—	45.8	—	—	2.5	—	48.0	46.5
5	Myristic, $C_{14}H_{28}O_2$	1.2	19.9	—	—	3.6	—	17.5	16.0
6	Palmitic, $C_{16}H_{32}O_2$	4.5	6.9	18.0	—	57.6	24.4	8.8	9.5
7	Stearic, $C_{18}H_{36}O_2$	—	Trace	42.3	2.0	1.8	35.4	2.0	3.0
8	Arachidic, $C_{20}H_{40}O_2$	—	—	1.1	—	—	—	—	—
9	Behenic, $C_{22}H_{44}O_2$	—	—	—	—	—	—	—	—
10	Lignoceric, $C_{24}H_{48}O_2$	—	—	—	—	—	—	—	—
	(b) Unsaturated Acids								
11	Myristoleic, $C_{14}H_{26}O_2$	—	—	—	—	—	—	—	—
12	Palmitoleic, $C_{16}H_{30}O_2$	—	—	—	—	—	—	—	—
13	Oleic, $C_{18}H_{34}O_2$	77.0	18.1	37.4	8.6	34.5	38.1	6.0	10.0
14	Linoleic, $C_{18}H_{32}O_2$	17.3	—	0.2	3.5	—	2.1	2.5	1
15	Linolenic, $C_{18}H_{30}O_2$	—	—	—	—	—	—	—	—
16	Elaeostearic, $C_{18}H_{30}O_2$	—	—	—	—	—	—	—	—
17	Ricinoleic, $C_{18}H_{34}O_3$	—	—	—	85.9	—	—	—	—
18	C_{20}-unsaturated, $C_{20}H_{38}O_2$.	—	—	—	—	—	—	—	—
19	C_{22}-unsaturated, $C_{22}H_{36}O_2$	—	—	—	—	—	—	—	—
20	Erucic, $C_{22}H_{42}O_2$	—	—	—	—	—	—	—	—
	(c) Constants								
21	Specific gravity, 15/15°C.	0.918–0.920	0.916–0.918 (25/25°)	0.852–0.860 (99/15°)	0.958–0.968	0.890 (50°)	0.973	0.917–0.919 (25°)	0.868–0.871 (99/15°)
22	Refractive index	1.453–1.459 (25°)	1.449–1.451 (40°)	1.456–1.457 (40°)	1.473–1.477 (25°)	1.456–1.458	1.453–1.458 (40°)	1.448–1.450 (40°)	1.449–1.450 (40°)
23	Iodine value	93–105	14–18	29–38	81–91	20–29	35–40	7.5–10.5	9–14
24	Saponification value	183–196	247–251	189–200	176–187	200–209	190–200	250–264	252–260
25	Unsaponifiable matter, %	0.8	Below 0.8	0.4–2.0	Below 1.0	0.5–1.5	Below 1.0	Below 0.5	Below 0.5
26	Titer, °C.	10–12	22–23	51–53	—	45–53	45–50	20–24	20–21
27	Melting point, °C.	—	24–26	34–39	—	52–55	28–36	23–26	18–24
28	Acetyl value	—	—	—	144–150	—	—	8	—
29	Reichert-Meissl value	Below 0.5	10–12	Below 0.5	Below 0.5	Below 0.5	Below 1.0	6–8	6.8–8.4
30	Polenske value	Below 1.0	—	Below 0.5	Below 0.5	Below 0.5	Below 0.5	12–18	12–16

[a] d = drying oil, sd = semidrying oil, nd = nondrying oil.

No.	Composition of fatty acids	Corn oil (sd)	Cottonseed oil (sd)	Hempseed oil (d)	Illipe butter (nd)	Japan tallow (nd)	Kapok oil (nd)	Linseed oil (d)	Murumuru palm kernel oil (nd)
	(a) Saturated Acids								
1	Caproic, $C_6H_{12}O_2$	—	—	—	—	—	—	—	1.1
2	Caprylic, $C_8H_{16}O_2$	—	—	—	—	—	—	—	1.6
3	Capric, $C_{10}H_{20}O_2$	—	—	—	—	—	—	—	12.6
4	Lauric, $C_{12}H_{24}O_2$	—	—	—	—	—	—	—	42.6
5	Myristic, $C_{14}H_{28}O_2$	—	0.5	—	—	—	—	0.2	36.8
6	Palmitic, $C_{16}H_{32}O_2$	7.5	21.0	} 10.0	23.7	77	10.2	5.6	4.5
7	Stearic, $C_{18}H_{36}O_2$	3.5	2.0		19.3	} 5.0	8.4	3.5	2.2
8	Arachidic, $C_{20}H_{40}O_2$	0.5	Trace	—	—	—	1.2	0.6	—
9	Behenic, $C_{22}H_{44}O_2$	—	—	—	—	—	—	—	—
10	Lignoceric, $C_{24}H_{48}O_2$	0.2					Trace	0.1	
	(b) Unsaturated Acids								
11	Myristoleic, $C_{14}H_{26}O_2$	—	—	—	—	—	—	—	—
12	Palmitoleic, $C_{16}H_{30}O_2$	—	—	—	—	—	—	—	—
13	Oleic, $C_{18}H_{34}O_2$	46.3	33.0	11.8	43.3	12	45.2	21.0	10.8
14	Linoleic, $C_{18}H_{32}O_2$	42.0	43.5	43.8	13.7	Trace	32.9	24.0	0.4
15	Linolenic, $C_{18}H_{30}O_2$	—	—	22.8	—	—	—	45.0	—
16	Elaeostearic, $C_{18}H_{30}O_2$	—	—	—	—	—	—	—	—
17	Ricinoleic, $C_{18}H_{34}O_3$	—	—	—	—	—	—	—	—
18	C_{20}-unsaturated, $C_{20}H_{32}O_2$.	—	—	—	—	—	—	—	—
19	C_{22}-unsaturated, $C_{22}H_{36}O_2$	—	—	—	—	—	—	—	—
20	Erucic, $C_{22}H_{42}O_2$	—	—	—	—	—	—	—	—
	(c) Constants								
21	Specific gravity, 15/15°C	0.922–0.926	0.916–0.918	0.929–0.934	0.856–0.870	0.965–0.990	0.920–0.933	0.931–0.938	0.920
22	Refractive index	1.470–1.474 (25°)	1.463–1.472 (25°)	1.472 (25°)	1.458–1.462 (40°)	1.455–1.458 (40°)	1.466–1.472 (25°)	1.477–1.482 (25°)	1.449–1.454 (40°)
23	Iodine value	103–128	99–113	150–166	53–70	5–17	86–110	170–204	11–13
24	Saponification value	187–193	189–198	190–193	188–204	209–220	189–197	188–196	237–247
25	Unsaponifiable matter, %	Below 2	Below 1.5	Below 1.5	0.8–3.5	0.5–2.0	0.5–1.8	Below 1.7	Below 1
26	Titer, °C	14–20	30–37	14–17	36–45	53–59	27–32	19–21	26
27	Melting point, °C				23–31	50–54			32–35
28	Acetyl value	10	7.5–12.5		3.3	—	7–13	4–10	3
29	Reichert-Meissl value	Below 0.5	Below 1.0		0.7–3.6	Below 1.0	Below 0.5		
30	Polenske value	Below 0.5	Below 1.0		0.9	—	Below 0.5		—

a d = drying oil, sd = semidrying oil, nd = nondrying oil.

TABLE XII-4 (*continued*)

VEGETABLE OILS AND FATS

No.	Composition of fatty acids	Mustard seed oil (Black) (nd)	Mustard seed oil (White) (nd)	Niger seed oil (d)	Olive oil (nd)	Olive kernel oil (nd)	Palm oil (Africa, Sumatra) (nd)	Palm kernel oil (nd)	Peanut oil (nd)
	(a) *Saturated Acids*								
1	Caproic, $C_6H_{12}O_2$		—	—	—	—	—	Trace	—
2	Caprylic, $C_8H_{16}O_2$	—	—	—	—	—	—	2.7	—
3	Capric, $C_{10}H_{20}O_2$	—	—	—	—	—	—	7.0	—
4	Lauric, $C_{12}H_{24}O_2$	—	—	3.3	—	—	1.0	46.9	—
5	Myristic, $C_{14}H_{28}O_2$	—	—		Trace	—	14.1	14.1	—
6	Palmitic, $C_{16}H_{32}O_2$	—	—	8.4	9.0	6.0	42.5	8.8	7.0
7	Stearic, $C_{18}H_{26}O_2$	2.0	2	4.9	2.3	4.0	4.0	1.3	5.0
8	Arachidic, $C_{20}H_{40}O_2$	Trace	1	0.5	0.2	—	—	—	4.0
9	Behenic, $C_{22}H_{44}O_2$	—	—	—	—	—	—	—	—
10	Lignoceric, $C_{24}H_{48}O_2$	2.0	1	—	—	—	Trace	—	3.0
	(b) *Unsaturated Acids*								
11	Myristoleic, $C_{14}H_{26}O_2$	—	—	—	—	—	—	—	—
12	Palmitoleic, $C_{16}H_{30}O_2$	—	—	—	—	—	—	—	—
13	Oleic, $C_{18}H_{34}O_2$	24.5	28	31.0	82.5	83	43.0	18.5	60.0
14	Linoleic, $C_{18}H_{32}O_2$	19.5	14.5	54.3	6.0	7	9.5	0.7	21.0
15	Linolenic, $C_{18}H_{30}O_2$	2	1	—	—	—	—	—	—
16	Elaeostearic, $C_{18}H_{30}O_2$	—	—	—	—	—	—	—	—
17	Ricinoleic, $C_{18}H_{34}O_3$	—	—	—	—	—	—	—	—
18	C_{20}-unsaturated, $C_{20}H_{32}O_2$.	—	—	—	—	—	—	—	—
19	C_{22}-unsaturated, $C_{22}H_{36}O_2$.	—	—	—	—	—	—	—	—
20	Erucic, $C_{22}H_{42}O_2$	50.0	52.5	—	—	—	—	—	—
	(c) *Constants*								
21	Specific gravity, 15/15°C.	0.914–0.923	0.913–0.916	0.924–0.927	0.914–0.919	0.918–0.919	0.921–0.925	0.860–0.873 (99/15°)	0.917–0.921
22	Refractive index	1.465–1.477 (25°)	1.468–1.474 (25°)	1.467–1.469 (40°)	1.466–1.468 (25°)	1.467–1.469 (25°)	1.453–1.456 (40°)	1.449–1.452 (40°)	1.467–1.470 (25°)
23	Iodine value	106–113	94–106	126–134	80–88	86–88	44–54	14–23	84–100
24	Saponification value ...	176–184	170–178	188–193	188–196	181–184	195–205	245–255	188–195
25	Unsaponifiable matter, %	Below 1.5	Below 1.5	0.5–1.2	Below 1.8	Below 2	Below 1	Below 1	Below 1
26	Titer, °C.	6–8	8–10	26	17–26	—	40–47	20–28	26–32
27	Melting point, °C.	—	—	—	—	—	27–50	24–26	—
28	Acetyl value	—	—	Below 1.0	4–12	—	15–23	—	8.5–9.5
29	Reichert-Meissl value	—	—	—	—	—	Below 0.5	4–7	Below 0.5
30	Polenske value	—	—	—	—	—	Below 0.5	9–11	Below 0.5

d = drying oil, sd = semidrying oil, nd = nondrying oil.

No.	Composition of fatty acids	Perilla oil (d)	Poppyseed oil (d)	Rapeseed oil (nd)	Safflower oil (d)	Sesame oil (sd)	Shea nut butter (nd)	Soybean oil (d)	Sunflower oil (sd)	Ucuhuba butter oil (nd)
	(a) Saturated Acids									
1	Caproic, $C_6H_{12}O_2$	—	—	—	—	—	—	—	—	—
2	Caprylic, $C_8H_{16}O_2$	—	—	—	—	—	—	—	—	—
3	Capric, $C_{10}H_{20}O_2$	—	—	—	—	—	—	—	—	0.5
4	Lauric, $C_{12}H_{24}O_2$	—	—	—	Trace	—	—	—	—	14.8
5	Myristic, $C_{14}H_{28}O_2$	—	—	—	1.1	—	—	—	—	72.8
6	Palmitic, $C_{16}H_{32}O_2$	7.5	7.0	1.5	2.9	8.5	5.7	6.5	3.5	4.9
7	Stearic, $C_{18}H_{36}O_2$	Trace		0.5	1.1	4.5	41.0	4.5	3.0	
8	Arachidic, $C_{20}H_{40}O_2$	—	—	—	Trace	0.6	—	0.7	0.6	—
9	Behenic, $C_{22}H_{44}O_2$	—	—	0.5	—	—	—	—	—	—
10	Lignoceric, $C_{24}H_{48}O_2$	—	—	1.0	Trace	—	—	Trace	0.4	—
	(b) Unsaturated Acids									
11	Myristoleic, $C_{14}H_{26}O_2$	—	—	—	—	—	—	—	—	—
12	Palmitoleic, $C_{16}H_{30}O_2$	—	—	—	—	—	—	—	—	—
13	Oleic, $C_{18}H_{34}O_2$	8.0	28.3	23.9	32.8	47.4	49.0	33.5	34.0	6.3
14	Linoleic, $C_{18}H_{32}O_2$	38.0	58.5	19.8	61.1	39.0	4.3	52.5	58.5	—
15	Linolenic, $C_{18}H_{30}O_2$	46.5	—	1.8	Trace	—	—	2.3	—	—
16	Elaeostearic, $C_{18}H_{30}O_2$	—	—	—	—	—	—	—	—	—
17	Ricinoleic, $C_{18}H_{34}O_3$	—	—	—	—	—	—	—	—	—
18	C_{20} unsaturated, $C_{20}H_{32}O_2$	—	—	—	—	—	—	—	—	—
19	C_{22} unsaturated, $C_{22}H_{36}O_2$	—	—	—	—	—	—	—	—	—
20	Erucic, $C_{22}H_{12}O_2$	—	—	—	—	—	—	—	—	—
	(c) Constants									
21	Specific gravity 15/15°C	0.930–0.937	0.924–0.927	0.913–0.918	0.925–0.928	0.920–0.926	0.916–0.918	0.924–0.928	0.922–0.926	0.871 (99 15)
22	Refractive index	1.480–1.482 (25°)	1.467–1.470 (25°)	1.470–1.474 (25°)	1.472–1.475 (25°)	1.470–1.474 (25°)	1.464–1.467 (40°)	1.474–1.476 (25°)	1.472–1.474 (25°)	1.456–1.461 (40°)
23	Iodine value	193–208	130–140	97–108	140–150	103–116	56–67	120–141	125–136	13–16
24	Saponification value	188–197	189–196	170–180	188–194	188–195	178–190	189–195	188–194	218–228
25	Unsaponifiable matter, %	Below 1.5	Below 1	Below 1	Below 1.5	Below 1.8	2–11	Below 1.5	Below 1.5	1.5–3.2
26	Titer, °C.	—	15–19	11–15	15–18	20–25	49–54	—	16–20	38–44
27	Melting point, °C.	—	—	—	—	—	32–42	—	—	42–47
28	Acetyl value	—	—	—	13	10	—	—	14–16	—
29	Reichert-Meissl value	—	Below 0.5	Below 1	Below 0.5	2.8	1.2–2.5	Below 1	Below 0.5	1
30	Polenske value	—	—	Below 0.5	—	—	Below 1	Below 1	Below 0.5	6

[a] d = drying oil, sd = semidrying oil, nd = nondrying oil.

TABLE XII-5

CHARACTERISTICS AND COMPOSITION OF NATURAL OILS AND FATS

No.	Composition of fatty acids	Butterfat (bovine)	Bone grease (commercial)	Horse fat	Lard	Neat's foot oil	Tallow (beef)	Tallow (mutton)	Commercial grease Composition similar to lard
	(a) *Saturated Acids*								
1	Butyric, $C_4H_8O_2$	3.0							
2	Caproic, $C_6H_{12}O_2$	1.4							
3	Caprylic, $C_8H_{16}O_2$	1.5							
4	Capric, $C_{10}H_{20}O_2$	2.7							
5	Lauric, $C_{12}H_{24}O_2$	3.7							
6	Myristic, $C_{14}H_{28}O_2$	12.1			1.3	5.0	3–7	5	
7	Palmitic, $C_{16}H_{32}O_2$	25.3	20–21	29.5	28.3	18.0	30	24–25	
8	Stearic, $C_{18}H_{36}O_2$	9.2	19–21	6.8	11.9	3.0	20–21	30	
9	Arachidic, $C_{20}H_{40}O_2$	1.3							
10	Behenic, $C_{22}H_{44}O_2$								
11	Lignoceric, $C_{24}H_{48}O_2$								
	(b) *Unsaturated Acids*								
12	Myristoleic, $C_{14}H_{26}O_2$	2.0			0.2				
13	Palmitoleic, $C_{16}H_{30}O_2$	4.0			2.7				
14	Oleic, $C_{18}H_{34}O_2$	29.6	50–55	55	48	79.0	45	36	
15	Linoleic, $C_{18}H_{32}O_2$	3.6	5–10	6–7	6.0		1–3	2–4	
16	Linolenic, $C_{18}H_{30}O_2$			1.7					
17	Elaeostearic, $C_{18}H_{30}O_2$								
18	Ricinoleic, $C_{18}H_{34}O_3$								
19	C_2-unsaturated, $C_2H_{32}O_2$.				2.1				
20	C_2-unsaturated, $C_2H_{32}O_2$.								
	(c) *Constants*								
21	Specific gravity, 15/15°C.	0.930–0.940	0.914–0.916	0.916–0.922	0.934–0.938	0.906–0.912 (25/25°)	0.943–0.952	0.937–0.952	
22	Refractive index, 40°C ...	1.453–1.456		1.462	1.459–1.461	1.458–1.461	1.454–1.458	1.454–1.458	
23	Iodine value	26–42	48–56	72–86	53–77	69–76	40–48	35–46	50–55 (darker grades 60–68)
24	Saponification value	210–233	186–198	195–199	190–202	190–199	190–199	192–197	185–195
25	Unsaponifiable matter, %	Below 0.5	Below 2	Below 0.8	Below 0.8	Below 0.8	Below 1	Below 1	1
26	Titer, °C.	33–38	38–42	34–38	33–43	20–30	40–47	43–48	38–42
27	Melting point, C.	28–35	21–22	36–43	33–46		40–48	44–51	39–44
28	Acetyl value	2–9		1.8–2.4	2.6	11	3–8		
29	Reichert-Meissl value	26–34		Below 2	Below 1	Below 0.5	Below 1		
30	Polenske value	1.5–3.5							

No.	Composition of fatty acids	Cod liver oil	Herring oil	Menhaden oil	Porpoise oil	Salmon oil	Sardine oil (commercial)	Whale oil
	(a) Saturated Acids							
1	Butyric, $C_4H_8O_2$	—	—	—	13–20	—	—	—
2	Caproic, $C_6H_{12}O_2$	—	—	—	—	—	—	—
3	Caprylic, $C_8H_{16}O_2$	—	—	—	—	—	—	—
4	Capric, $C_{10}H_{20}O_2$	—	—	—	—	—	—	—
5	Lauric, $C_{12}H_{24}O_2$	—	—	—	3–4.5	—	—	—
6	Myristic, $C_{14}H_{28}O_2$	4–6	7.0	7 0	12 14	2.2 5.0	5.0	8.0
7	Palmitic, $C_{16}H_{32}O_2$	7–10	8.0	16.0	7	15.0	14.0	11.0
8	Stearic, $C_{18}H_{36}O_2$	Trace	Trace	1 0	Trace	4.0	3.0	2.5
9	Arachidic, $C_{20}H_{40}O_2$	—	—	—	—	—	—	—
10	Behenic, $C_{22}H_{44}O_2$	—	—	—	—	—	—	—
11	Lignoceric, $C_{24}H_{48}O_2$	—	—	—	—	—	—	—
	(b) Unsaturated Acids							
12	Myristoleic, $C_{14}H_{26}O_2$	0.5	Trace	Trace	3.0	Trace	Trace	1.5
13	Palmitoleic, $C_{16}H_{30}O_2$	17	18.0	17.0	25.0	9.0	12.0	17.5
14	Oleic, $C_{18}H_{34}O_2$	} 25–30	9.0	27.0	} 20.0	} 27.0	10.0	34.0
15	Linoleic, $C_{18}H_{32}O_2$		13.0	Trace			15.0	9.0
16	Linolenic, $C_{18}H_{30}O_2$	—	—	—	—	—	—	Trace
17	Elaeostearic, $C_{18}H_{30}O_2$	—	—	—	—	—	—	—
18	Ricinoleic, $C_{18}H_{34}O_3$	—	—	—	—	—	—	—
19	C_{20}-unsaturated, $C_{20}H_{32}O_2$	25	20.0	20.0	15	—	22.0	5.0
20	C_{22}-unsaturated, $C_{22}H_{36}O_2$	10	25.0	12.0	6.5	—	19.0	12.0
	(c) Constants							
21	Specific gravity 15/15°C	0.922–0.932	0.920–0.936	0.925–0.936	0.926	0.924 0.926	0.926–0.934	0.917 0.927
22	Refractive index, 40°C.	1.474–1.478	1.470–1.476	1.470–1.478	1.463	1.475–1.477	—	1.470 1.477
23	Iodine value	(25°)	(25°)	(25°)	(25°)	(25°)	—	(25°)
24	Saponification value	140–170	124–128	148–160	119	141 166	170–193	110–135
25	Unsaponifiable matter, %	180–190	179–194	189–193	195	183–186	189–193	185–194
26	Titer, °C.	Below 2	2–3	—	Below 4	—	Below 2	Below 2
27	Melting point, °C.	18–24	—	—	—	—	27–28	22 24
28	Acetyl value	—	—	—	—	—	—	—
29	Reichert-Meissl value	4.8	—	—	47	—	—	—
30	Polenske value	Below 2	Below 1	Below 1.5	—	Below 1	—	0.7 2.4

unsaturated fatty acids are usually solid at ordinary temperatures. Further-more, oils with a high amount of unsaturated fatty acids (*e.g.*, linseed oil) are likely to dry when exposed in a thin layer to light and air. In the fol-lowing classification, the words *nondrying, semidrying,* and *drying* occur which denote this property of an oil. They usually apply to oils of vegetable origin. Unsaturation of an oil or fat is shown by the iodine value (Chapter XXXVIII, 7) which gives the amount of iodine chemically absorbed by the fat molecule in grams per 100 grams of oil or fat. Every double bond in the fat molecule is responsible for the absorption of two atoms of iodine. Tables XII-4 and XII-5[2a] give detailed information on the properties and composi-tion of the most important fats and oils used in the soap industry.

The soap industry, however, has to classify its fatty raw materials in a somewhat different manner in order to denote the properties of the soap pre-pared from them. Furthermore, the soapmaker is interested especially in the saponification value, which shows him the amount of alkali he has to use for complete saponification of the fat stock. The saponification value (see Chap. XXXVIII, 6) gives the amount of KOH (mg.) required to saponify 1 g. of oil or fat. This value still does not give directly the actual amount of caustic soda required. This is simply calculated by multiplying the saponification value by 40/56.1. Table XII-6 gives the saponification value and parts of NaOH, etc., per 100 parts oils and fats and their fatty acids. If the com-position of the fatty material is compared with saponification value, it is found that the higher the percentage of fatty acids with a lower molecular weight, the higher is the saponification value. This accounts for the fact that coconut oil needs more alkali for saponification than does tallow.

In classifying fats and oils according to the properties of the soaps they yield, roughly five groups of soap fats and oils can be distinguished:

(*1*) *Hard fats giving slow lathering soaps.* This group includes tallow, garbage greases, hydrogenated marine and vegetable oils with a high melting point and titer, and palm oil. These fats form soaps with low lathering power in cold water, improving in warm water. They are mild on the skin and have good cleansing effect in spite of their slow lathering. As a group, they constitute about 60% of the total amount of fats used in the soap industry. Tallow alone constitutes about 40% of all soap fats.

(*2*) *Hard fats giving quick-lathering soaps* (or *the lauric group of fats*). These comprise, coconut oil, palm kernel oil and babassu oil. The soaps made from the lauric group are less sensitive to electrolytes (see Chap. V, 1), *e.g.*, common salt, and are thus suitable for the manufacture of *marine soap*, which lathers even in sea water. On the average, more than 15% of fats going into the soap kettles of United States soap factories are of this group, over 90% of which is coconut oil.

(*3*) *Oils giving soaps of soft consistency.* In the United States, olive oil, soybean oil, and a certain amount of groundnut oil (peanut oil) are the more important of this

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[2a] Constants taken mainly from tables by the A.O.C.S. For more detailed informa-tion with regard to the composition of fats and oils see A. E. Bailey, *Industrial Oil and Fat Products*, 2nd ed., Interscience, New York, 1951.

group. Linseed oil is used mainly for the production of soft potash soap. Here, it must be mentioned that the classification is somewhat incorrect for olive oil. It is possible to produce a very hard and brittle soap purely from olive oil if certain conditions during the soap-boiling process are observed, namely, a strong salting-out on spent lye (see Chap. V, 1 and XVIII, 1). Of the "soft fat" group, an average of 12% of all soap fats used in the U. S. belong to the soft fat group. Marine oils (whale oil) also belong to this group of soap oils. Some of the fats and oils of this group are of the semidrying or drying types,

TABLE XII-6

	Oil or fat		Fatty acid from corresponding oil or fat			
Oil or fat	Mean sapon. value	Av. amt. of NaOH for sapon.. % NaOH	NaOH (approx.) needed/100 kg. fatty acid, kg.	Na$_2$CO$_3$ (approx.) needed/100 kg. fatty acid, kg.	KOH (approx.) needed/100 kg. fatty acid, kg.	K$_2$CO$_2$ (approx.) needed/100 kg. fatty acid, kg.
Linseed oil	193	13.8	14.7	19.5	20.8	25.2
Hemp oil	192	13.7	14.4	19.1	20.5	24.9
Sunflower oil	193	13.8	14.7	19.5	20.8	25.2
Maize oil	191	13.6	14.7	19.5	20.8	25.2
Soya bean oil	192	13.7	14.7	19.5	20.8	25.2
Cotton oil	194	13.9	14.8	19.6	20.9	25.4
Ground nut oil	193	13.8	14.7	19.5	20.8	25.2
Sesame oil	190	13.6	14.7	19.5	20.8	25.2
Castor oil	181	13.0	13.7	18.1	19.2	23.7
Colza oil	179	12.8	13.7	18.1	19.2	23.7
Olive oil	192	13.7	14.6	19.4	20.7	25.1
Neatsfoot oil	194	13.9	14.7	19.5	20.8	25.2
Sardine oil	191	13.6	14.7	19.5	20.8	25.2
Whale oil	188	13.4	14.1	18.6	19.7	24.2
Cotton stearin	195	14.0	14.7	19.5	20.8	25.2
Palm oil	199	14.2	14.9	19.7	21.0	25.5
Vegetable tallow	200	14.3	15.0	19.8	21.1	25.6
Bone fat	195	14.0	14.5	19.2	20.6	25.0
Lard	191	13.6	14.7	19.5	20.8	25.2
Tallow	198	14.1	14.9	19.7	21.0	25.5
Palm kernel oil	248	17.7	18.9	24.9	26.4	32.5
Coconut oil	253	18.1	19.7	26.0	27.6	33.8
Babussu oil	248	17.7	18.9	24.9	26.4	32.5

which readily undergo changes under the influence of air or light or during storage. The soaps made from these oils are more liable to rancidity and discoloration than soaps made from tallow and fats of the lauric group (see Chapter XXXI).

(4) *Rosin.* Rosin comprises a group in itself. This raw material will be discussed in a more detailed manner when describing the individual fats and oils. Soaps prepared from rosin lather quickly and dissolve readily, but are too soft to permit them from being used alone. However, it is often used with advantage as a portion of the fat stock.

(5) *Synthetic fatty acids and naphthenic acids.* These will be dealt with later.

Table XII-7 shows the characteristics of soaps made from various fats. This table deals with the characteristics of soap made from only *one* fat or

oil and it is readily understood that none of the individual fats produces the
ideal soap. But with a knowledge of the characteristics of soaps made from
individual fats and oils, the soapmaker can achieve a soap that approaches
the ideal by blending the available stocks. Thus, in a combination of tallow
and coconut, the latter will contribute solubility and lathering quality, while
the former will contribute mildness and long-lasting lather. The character-
istic of rancidity prevalent in cottonseed oil soap will diminish when mixed
with tallow and coconut oil. However, the properties of individual soap fats
set certain limits on the combinations that may be used technically for the
production of a specified soap, but they leave a wide range of combinations
open to the manufacturer within which he may substitute one fat for an-
other, particularly if the fats belong to the same group. Furthermore, his
choice of the pan charge is influenced by the price situation of the market.

The soap industry is the largest consumer of inedible fats. Inedible tal-
low, for instance, comprises approximately 20% of all edible and inedible
fats and oils used in the United States and almost 90% of the inedible tallow
produced goes into the soap kettle. This single fat constitutes almost 50%
of all fats and oils used in the industry. Of course, edible fats and oils are
used in the soap industry as well. Their use is determined, to a large extent,
by price and market conditions. Following are classifications and definitions
for inedible fats and oils.[4]

    1. Fats which are too unattractive for human consumption in taste, odor, color, or
       other physical and chemical characteristics because of:
       a. The mode of extraction, as, for instance, steam-rendered tallow, which has
         an undesirable odor.
       b. Unpleasant origin, i.e., extracted from garbage and sewage, tankage, or con-
         demned animals.
       c. Their inherent characteristics, as, for instance, the odor of fish oils.
    2. Fats which are dangerous to public health because they are:
       a. Carriers of disease transmittable to man and condemned as such by federal
         inspectors.
       b. Made intentionally poisonous for human consumption, as, for instance,
         palm kernel oil, denatured in order to save import duties. (Under the
         U.S. tariff act of 1930, palm kernel oil was permitted free of duty if dena-
         tured.)
       c. Poisonous for human consumption due to mode of extraction, as, for in-
         stance, olive oil foots.
    3. Fats coming from certain parts of animals, arbitrarily classed as inedible or, as
       we want to add, animal fats which have become strongly rancid and evil-smelling
       during prolonged or unsuitable storage or otherwise.
    4. The foots of the vegetable oil industry.

[3] G. Hefter and H. Schönfeld, Chemie und Technologie der Fette und Fettprodukte,
Vol. 4 (Seifen und Seifenartige Stoffe), Springer, Vienna, 1937.
    [4] A. Kozlitz and P. Diebold, "The Demand for Fats and Oils in the Soap Industry,"
Agr. Expt. Sta., Ames, Iowa, Research Bulletin No. 311, 1943.

TABLE XII-7. Some Oils and Fats and the Characteristics of Their Sodium Soaps[3]

Soap	Color	Consistency	Odor	Foam	Detergent quality	Skin reaction	Use	Saponification	Av. theor. yield of glycerine on neutral fat or oil	Salt soln. for complete salting-out (NaCl)
Coconut oil	White to yellowish	Very hard, brittle	Practically odorless	Quick big bubbles, short lasting	Good also in cold water	Makes skin rough	All kinds of soaps, especially toilet, with tallow or stearic acid, shaving soap	Quick with strong lye	14%	20° Bé
Palm kernel oil	Yellowish-white to yellow-grey	Same	Same	Same	Same	Same	Household and toilet soap, s. powder	Same	13.5%	Same
Babassu oil	Same	Same	Same	Same	Same	Same	Same	Same	13.5%	Same
Palm oil (refined)	Yellowish	Very hard	Similar to oil, like violet	Slow, small bubbles, lasting	Very good	Very mild	Same	Fairly easy with lyes 10–15° Bé	11%	3° Bé
Olive oil	Yellow to drab green	Hard	Weak, similar to oil	Fairly good	Good	Same	Household, textile, and toilet soap	According to FFA content	10.5%	5.5 Bé
Peanut oil	Light yellow	Hard on spent-lye, softer on niger	Practically odorless	Same	Fairly good	Same	Same	Fairly easy with lyes 15–18° Bé	10.5%	Same
Soybean oil	Light yellow to green	Hard	Same	Mediocre	Mediocre	Same	Same	Fairly easy with weak lyes 10–12° Bé	10.5%	6° Bé
Tallow	White to yellowish-white	Very hard	Practically odorless. lower grades like fat	Slow, small bubbles, lasting	Good	Same	Household, textile, toilet, shaving soap	Rather difficult, with weak lyes	11%	5° Bé
White grease (lard)	White	Hard	Odorless	Easy, small bubbles, lasting	Same	Same	Household, flakes, toilet soap	Same	11%	6° Bé
Whale oil	Yellow brown	Fairly soft	Fishy	Small bubbles, lasting	Fairly good	Mild	Soft soap	Easy with lyes 10–12° Bé	11%	5.5° Bé
Cottonseed oil	Grayish-white to dirty yellow	Same	Similar to oil	Mediocre, but lasting	Good	Same	Household soap	Refined oil difficult to sap'y.	10.6%	Same

As already mentioned, about 90% of inedible tallow goes into the soap kettle (since the candle industry has lost its importance as a consumer of tallow). About 50% of grease goes into the industry, the remaining 50% being used mainly for the manufacture of lubricating greases. The "foots" of vegetable oils have a similar outlet as raw material for the soap industry and for the manufacture of lubricating grease.

(3) The Deterioration of Fats and Oils

Fats and oils are liable to deterioration by rancidity. The chief form which rancidity takes is oxidation. It is not necessary for great percentages of the oil or fat to undergo oxidation changes during the development of rancidity. Not more than 0.1% of the fat need actually decompose to form the volatile, low molecular weight compounds responsible for its rancid flavor and odor.[5]

The oxidation of a fat or oil proceeds, first by the addition of oxygen at or near the double bond of a fatty acid chain. Unstable peroxides or hydroperoxides, are formed. For a more detailed discussion of the modern concepts regarding the mechanism of rancidification, we refer to Lea and to Bailey.[6]

Whatever the structure, the peroxides are but intermediate and transitory products in the general course of oxidation. They are highly reactive, and decompose quickly or combine with one another in a variety of poorly understood reactions, to yield the compounds actually responsible for rancid flavors and odors.

The position and number of double bonds have a considerable effect on the readiness of an oil to become rancid and on the further change of the peroxides formed. The further chemical change of the peroxides is responsible for the formation of aldehydes of medium molecular weight and particularly heptylic and nonoic aldehydes. Such compounds may be formed by oxidation and rupture of a fatty acid chain at a double bond:

$$
\underset{\substack{\text{Unsaturated}\\\text{glyceride}}}{CH_3(CH_2)_xC\!=\!C\!-\!R} + O_2 \rightarrow \underset{\text{Peroxide}}{CH_3(CH_2)_xC\!-\!C\!-\!R} \rightarrow \underset{\text{Aldehydes}}{CH_3(CH_2)_xC + C\!-\!R}
$$
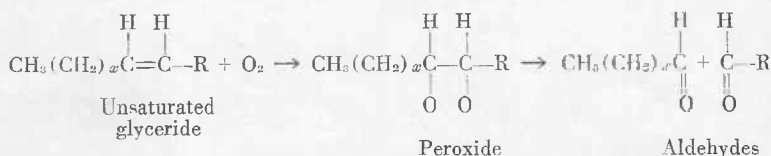
Many other substances, including low molecular weight aldehydes and acids, hydroxy acids, keto acids, and ketones, are found in rancid fats, but it is not

[5] J. Pritzker and R. Jungkunz, *Z. Untersuch. Lebensm.*, 57, 419–421 (1929).

[6] C. H. Lea, *Rancidity in Edible Fats*, Dept. Sci. Ind. Research Food Invest., Special Rept. No. 46 (1939). A. E. Bailey, *Industrial Oil and Fat Products*, 2nd ed., Interscience, New York, 1951.

believed that any of these contribute in any important way to the typical flavor and odor. The amount of oxygen required to produce rancidity varies considerably according to the composition of the oil, the presence or absence of antioxidants or prooxidants, and the conditions under which oxidation is carried out. Fats high in oleic acid and low in linoleic acid become rancid after the absorption of less oxygen than fats in which the ratio of these acids is reversed. The rate of oxygen absorption by a fat is accelerated by heat and by exposure to light (particularly ultraviolet). Hydrolysis does not necessarily, or even usually, accompany the oxidation of a fat. Therefore, the free fatty acid content of a fat does not indicate the presence or absence of rancidity.

When the course of oxidation of a fat is followed experimentally, either by measuring the amount of oxygen absorbed, or by determining the peroxide value of the fat, it is found that the course of oxidation exhibits two distinct phases. During the initial phase—the induction period—oxidation proceeds at a relatively slow, and more or less uniform, rate. Then, after a certain critical amount of oxidation has occurred, the reaction enters a second phase characterized by a rapidly accelerating rate of oxidation, and an eventual rate many times greater than that observed in the initial phase. The point at which the sample begins to smell and taste rancid coincides with the early part of the second phase.

There exist organic compounds—natural constituents of fats and oils, as well as other organic compounds—which improve the stability of oils and fats against rancidity, and these substances are especially important for the edible oil and fat industry; but it is important to note that antioxidants may have a very undesirable effect on the soap produced from such fats and oils. Hydroquinone has a very marked antioxidative effect, but it tints soap with an unpleasant brown color (Chap. XXXI, 4). Rancidity occurs in the soap as well, and is not necessarily caused by the presence of unsaponified fat or oil (see Chapter XXXI).

Rancidity in fats and oils may also develop from the action of microorganisms. These may cause very disagreeable rancidity, especially if tissue substances in crude or insufficiently refined tallow or grease start to decompose and ferment. Furthermore, triglycerides of lower molecular fatty acids, e.g., in coconut or palm kernel oils, are prey to a special form of rancidity (caused by microorganisms) called *ketone rancidity*,[7] which is characterized by a distinctive but not always unpleasant "esterlike" odor and a pungent, unpleasant taste; it was recognized (under various names) for many years before the mechanism of its production was understood. "Haller and Lassieur[7a] had identified methyl heptyl and methyl nonyl ketones, together

[7] C. H. Lea, *Rancidity in Edible Fats*, H. M. Stationery Office, London, 1938, pp. 56–60.

with smaller quantities of methyl undecyl ketone and of methyl heptyl and methyl nonyl carbinols, in the strongly smelling oil recovered during the commercial deodorization of crude coconut oil with steam. These must have been produced during drying of the copra or during storage of the oil, since coconut oil expressed from the fresh nut has a mild, agreeable, almondlike odor and taste. However, in 1921, Stokoe[7b] appears first to have definitely attributed "perfume" rancidity in coconut oil and in butter and margarine to the presence of ketones rather than of aldehydes or esters, and to have shown that these are produced by a particular group of microorganisms. Later investigators of this defect, particularly in coconut oil, have confirmed the finding that the characteristic odor developed is due to the action of molds, mainly *Penicillium* and *Aspergillus*, on the fat in the presence of moisture and nitrogenous material."[7c]

Here again the cause is the presence of organic substances from the tissue of the fruit which has remained in the oil. Strong refining would remove these substances together with products of rancidity already in the oil.

It should be pointed out here that for the use of fats and oils for the manufacture of soaps, even strong rancid oils and fats may be prerefined in order to become useful raw materials for the soap industry.

[7a] A. Haller and A. Lassieur, *C. r. acad. sci. Paris, 150*, 1013 (1910) ; *151*, 697 (1910).

[7b] E. N. Stokoe, *Biochem. J., 22*, 80 (1910) ; *J. Soc. Chem. Ind., 53*, 345T (1934).

[7c] O. Acklin, *Biochem. Z., 253* (1929).

REFINING OF OILS AND FATS*

Refining oils and fats for use in the soap industry is for the purpose of removing free fatty acids, mucilage, and coloring matter. It is not necessary to remove volatile odoriferous substances from an oil for the soap pan. Only in the case of fish oil and other strong-smelling oils and fats may a deodorization process be desirable (see Chapter XIII, 4).

(1) Desliming of Oils and Fats

The mucilaginous substances are removed by the action of dehydrating chemicals, mainly concentrated sulfuric acid. This process, very often used in the soap factory itself if a crude oil is to be pretreated, calls for much care and experience.[8] 0.75 to 1.5% of concentrated sulfuric acid, 66° Bé, is run slowly into the oil contained in an acid-resistant kettle of iron or other material, equipped with stirring gear and preferably cooled to 15 to 20°C. During this operation the oil is thoroughly stirred. The sulfuric acid has a coagulating action whereby dissolved products, such as mucilage, are precipitated. If too much acid is present, or if it acts for a prolonged time, it attacks the oil itself. The acid also inactivates the enzymes, which may be responsible for decomposition and rancidity of the oil.

At first the oil is colored green by the acid, but later it becomes jet black. A drop placed on a porcelain plate appears to be light colored, with inter-

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* A discussion of the extraction of oils and fats is considered to be outside the scope of this book. For a modern treatment of extraction methods, see Bailey, *Industrial Oil and Fat Products,* 2nd ed., Interscience, New York, 1951.

[8] J. Davidsohn and A. Davidsohn, *Soap, Perfumery and Cosmetics, 11,* 794–798 (1938).

spersed dark flakes.   After 4–5 hours the flakes settle out completely when
some water is added and the oil is left to clarify further.   The upper layer
consists of oil purified in this manner; the lower layer consists of the decom-
posed proteins, with a certain amount of oil remaining mixed with unchanged
sulfuric acid (the latter may sometimes be seen in a separate layer at the
bottom).   This deposited oleaginous layer can also be worked up to tech-
nical products, among which the organic sulfo acids are particularly im-
portant.

Sometimes oils are deslimed by treating the crude oils with the bleaching
earth used for bleaching alkali-refined oils (Chap. XIII, 3, B).   By this proc-
ess, no additional loss of oil occurs, since the oil which was absorbed by the
bleaching earth is added together with the earth.   Often a small amount of
water makes the process of desliming more efficient.   Certain oil impurities,
such as phosphatides, proteins, or protein fragments, and gummy or muci-
laginous substances, are soluble in the oil only in an anhydrous form, and
can be precipitated and removed if they are hydrated.   A small amount of wa-
ter is dispersed in the oil by vigorous stirring at slightly elevated temperature
(about 40°C.).   The process may be a continuous one, in which case the wa-
ter and oil are emulsified together in a continuous mixing device, and after a
suitable holding time the hydrated substances and the excess water are re-
moved by continuous centrifugation.   In some cases a weak solution of so-
dium carbonate, sodium bicarbonate, trisodium phosphate, or other non-
caustic alkali is substituted for the water, and the use of sodium chloride solu-
tion, boric acid, phosphoric acid, and other weak acids, etc. has also been
suggested in various patents.

The hydration process is employed especially for soybean and corn oil
and sometimes for cottonseed, peanut, and sunflower oils as well.   The hydra-
tion method of refining is not generally used on animal fats, since these fats
are for the most part substantially free of phosphatides or other hydratable
substances.   It has some application, however, in the treatment of dry-ren-
dered fats for the removal of dissolved or dispersed proteinous substances.

(2) Neutralization of Free Fatty Acids

The purpose of refining with caustic lyes is to remove free fatty acids and
remaining mineral acids from any previous acid treatment.   Both dilute and
more concentrated lyes are used, chiefly caustic soda.   It must be pointed out,
however, that in some very obstinate cases a much better bleaching action
has been obtained by neutralization with strong caustic potash than with
caustic soda.   The lye is run in from a raised kettle through a sprinkler into
the stirred oil.   The initial temperature is about 40°C., which is then increased
to about 60 to 70°C.   Samples are taken from time to time to see whether the

precipitated foots have acquired the desired settling characteristics. In that case the stirrer is shut off, and the mass left for 10 to 24 hours. The clarified oil is run off into a second vessel, where it is kept for some time at 40 to 50°C., and washed with warm water or common salt solution (10° Bé). It is then ready for filtration or drying (Fig. XIII, 1).

The effect of the caustic lye is primarily to neutralize the free fatty acids in the oils to form alkali soaps (soapstock). These absorb mechanically the coloring matters in the oils and other impurities. The bleaching action is based upon the latter effect. The alkali treatment naturally results at the same time in the formation of practically neutral oils.

For many purposes in the soap industry, the bleaching action in the course of alkali treatment is adequate, and a supplementary bleach of the neutralized oil with bleaching earth (see below) is unnecessary. In that case, the soapstock need only be allowed to settle, when the oil can be transferred to the soap kettle without being washed. The soapstock is extremely well adapted to the production of the darker grade bar soaps, and powders. Treatment of oils and fats with lye is, indeed, the simplest operation of all for the soap industry, because no special outlay on chemicals, etc. is required. Oils or fats treated with alkali are particularly suitable for the production of toilet soaps, owing to the exceptional stability of these soaps.

Neutralization may be carried out as follows. The temperature during neutralization depends to a large extent on the melting point of the fat, e.g., tallow is heated with steam in a closed or hooded kettle to a temperature of 99–100°C. (210–212°F.). Vegetable oils are neutralized at considerably lower temperatures (45–60°C.). Before the caustic soda is added it is desirable to shut off the steam and allow the excess water to settle so that it may be drawn off at the bottom. Enough caustic soda is then added to neutralize completely the free fatty acids. The strength of the caustic solution varies with the percentage of fatty acids being removed, 8° Bé being effective with low fatty acid. With increasing percentages of fatty acids, the strength of the caustic solution is advantageously raised to as much as 12° or 14° Bé. Soapstock settles to the bottom of the tank and is removed. The refined tallow is washed with hot water and, after settling overnight, any remaining soap solution is drawn off from the bottom.

In recent years, continuous processes for refining have become well established. The Sharples continuous process[9] for continuous refining by caustic soda is of note. The crude fat is fed by a centrifugal pump through a proportionometer, which is constructed so that the rate of flow of the oil regulates the flow of caustic soda. The two are then mixed in a small tank, the re-

[9] E. H. James, Oil & Soap, 11, 137 (1934). F. M. James (to Sharples Specialty Co.), Brit. Pat. 407,995 (1934), French Pat. 743,449 (1933), Canad. Pat. 355,720 (1936), U. S. Pat. 2,050,844 (1936).

Solvent conditioner

Solvent fractionation column

Solvent feed to column

Oil feed to column

Feed oil conditioner

Reflux conditioner

Reflux feed to column

Dry solvent vapor

Evaporator Condenser

Raffinate solution

Raffinate solution evaporator

Raffinate solution preheater

Extract solution evaporator

Extract solution preheater

Extract solution

Concentrated extract

Extract oil stripper

Sup'rn't'd steam

Stripper condenser

Wet solvent vapor

Solvent drier condenser

Wet solvent vapor

Water still condenser

Wet solvent vapor

Concentrated raffinate

Raffinate oil stripper

Sup'rn't'd steam

Decanting tank

Water Layer

Solvent Layer

Sup'rn't'd steam

Water Layer Still

To sewer

Solvent drier

Steam

Extract cooler

Raffinate cooler

Solvent storage

Feed oil storage

Extract storage

Raffinate storage

Fig. XIII-1. Flow sheet for a complete oil refining plant with solvents.[11]

sulting emulsion is forced through a tubular hot water heater where the temperature is raised to 50°C., and is then separated by a centrifuge. Washing with water is accomplished in the same manner. The refining losses are about 30% below that of the batch process. The contact time of lye and fat in the mixer is about 50 seconds, and in the heater about 4 minutes. Another continuous process uses a combination of caustic soda and soda ash.[10] Centrifuges are also used in this process for separating the soap stock.

Other deacidification processes have been proposed which extract the free fatty acids from the neutral oil or fat with solvents in which the neutral glycerides are relatively insoluble, e.g., alcohols, furfural, and propane. The Solexol process, using propane at various pressures, can selectively classify an oil into various fractions, including a color fraction, with a high degree of economy over normal bleaching and refining processes and promises to become more important with use. Developed by the M. W. Kellogg Co. and licensed by them, it is in commercial use in the United States for tallow refining for soapmaking purposes.

The use of furfural has recently found commercial application in the United States and promises wide applications.[11]

The *steam deacidification process* has found wide application in Europe. In this process the fatty acids are steam distilled out of the oil under certain conditions (*e.g.*, in vacuum). The advantage of the latter process is that the oil and fatty acids are isolated at once as such, there being no necessity to separate the soapstock at first, and then wash the oil. It is a disadvantage of the process that scarcely any bleaching action occurs during deacidification. Processes of this type are, in any case, only economically feasible in larger factories. The process is mainly suitable for the removal by the steam distillation of higher percentages (more than 25%) from oils and fats. It is thus especially suited for the refining of palm oil. As the process is in principle a fatty acid distillation process, it will be described under the fatty acids (see Chapter XV, 2).

(3) Bleaching of Oils and Fats

Very often, special bleaching processes are employed for removing color. A fundamental distinction is drawn between the two main bleaching methods: chemical and adsorption.[11a]

(A) BLEACHING WITH CHEMICALS

(1) Oxidation bleaching with air, hydrogen peroxide, chlorine, potas-

[10] B. Clayton (to Refining Co.), U. S. Pats. 2,190,593–4 (1940). See also M. K. Schwitzer, *Continuous Processing of Fats*, Leonard Hill, London, 1949 pp. 130–148.

[11] S. W. Gloyer, *Ind. Eng. Chem., 40*, 228 (1948).

[11a] J. Davidsohn, *Das Bleichen der Öle, Fette, Wachse und Seifen*, Borntraeger, Berlin, 1931.

siumbichromate, potassium permanganate, sodium chlorate, and organic oxidizing agents such as benzoyl peroxide.

(2) *Reduction bleaching*, especially with sulfurous acid or its salts, and salts of hydrosulfurous acid. These salts are generally used in conjunction with dilute sulfuric acid. Reduction bleaching is very rarely used for bleaching oils and fats, but oxidation bleaching is used extensively for the treatment of soda oils.

The principal steps in bleaching with hydrogen peroxide are as follows. 1–2% by weight of hydrogen peroxide (100 volumes strength) is added to the oil, which is maintained at a temperature of 160°F. for 3–6 hours. This is best achieved by blowing a vigorous stream of air through the heated oil, a process which exerts an additional oxidizing and bleaching effect and aids the work of the hydrogen peroxide. The use of higher concentrations of hydrogen peroxide, from 40 to 60% by volume, has been claimed to produce a more complete bleach.

In order to bleach with benzoyl peroxide, oil is heated to a temperature of 160°F., and 0.25 to 1% of benzoyl peroxide is added.[11b] The oil is maintained at this temperature with constant agitation until bleaching is complete —in approximately 3 to 6 hours. Agitation with air may be used to advantage. This process appears to require a certain amount of practical experience to enable correct amounts of benzoyl peroxide to be employed in different batches of oil. Variations in the color of the oil necessitates the use of different quantities of bleaching agent, and it must be borne in mind that too little benzoyl peroxide will result in a pale green soap, whereas an excess will cause a reddish tint to appear. Benzoyl peroxide is described as the most efficient decolorizing agent for emerald green oils, and it is stated that ten times as much active oxygen is necessary when chlorates and acid are used as when benzoyl peroxide is the bleaching agent.

An example to illustrate the range of peroxy compounds that may be employed in the bleaching of soapmaking oils is the use of sodium perpyrophosphate.[12] The method comprises treatment of such materials as bone fat or cottonseed oil by heating to 50–100°C. and then agitating while slowly adding a perpyrophosphate sufficient to bleach the material. Agitation is continued and the temperature is maintained until the bleaching is effected. Bleaching with other oxidation compounds is less often used for pretreatment of soap oils and a detailed description is therefore superfluous.

A very recent development in oxidation bleaching is bleaching with sodium chlorite, a method especially suitable for bleaching fatty acid stock, but

[11b] J. Davidsohn, *loc. cit.*, pp. 162–165.
[12] A. Noder, U. S. Pat. 2,250,203 (to Buffalo Electro-Chemical Co.).

also applicable to crude tallows and greases used for soap manufacture.[13] The process may be used either on the crude tallow or on the grease without any previous neutralization of free fatty acids. In this case, tallow is heated to 99–100°C. (210–212°F.) and treated with 1% by weight 66° Bé sulfuric acid (1 : 1 with water), plus 0.1% sodium chlorite in a 10% aqueous solution. The mixture is agitated for 1 hr., heated to 104–5°C. (220°F.) to remove moisture, treated at this temperature for 15 min. with acid-treated clay, and finally filtered. When refined tallow is used, it is heated with steam to a temperature of 99 to 100°C. (210–212°F.). Agitation with steam is continued and 1 lb. of technical sodium chlorite is added per 1,000 lbs. of tallow, followed by portions of a 20% aqueous solution of sulfuric acid until the pH of the water layer (which is equivalent to 10% of the weight of the tallow) in the kettle is 4 or less. Bromphenol blue (available in paper strips or in solution) is very convenient and sufficiently accurate as an endpoint indicator. The transition from purple to yellow shows that sufficient sulfuric acid has been added to activate all of the sodium chlorite. After pH 4 has been reached, steam agitation is continued for half an hour. The water is again checked to guard against an unforeseen rise in pH value; at the same time a check on the bleaching properties of the water layer is made with starch iodine paper—which should turn blue. The desired bleaching effect has usually been reached at this point. Steam is shut off and the water content of the kettle is raised by the addition of small amounts of a weak caustic soda solution (8° Bé) to a pH value of approximately 8. The water settles to the bottom and is drawn off. The bleached tallow is dried and allowed to rest a short time so that the sludge may settle to the bottom, from where it can be removed. Failure to bring the pH value back to 8 may result in reversion of color in the drying or in subsequent action of the acid on iron tank cars. This method is called the *acid activation* process.

Another method—the *chlorine activation* method—is carried out on the neutralized tallow as follows. Tallow is first refined as in the acid operation. A batch of refined tallow is heated with steam to 99–100°C. in a closed or hooded kettle and enough chlorine gas is added to the water layer (again representing about 10% of the weight of the tallow) to lower its pH to 6. Then 0.1% by weight of sodium chlorite, based on the weight of the tallow, is added. The chloride may be added as a 1–2% aqueous solution, or it may be more convenient to add the water first and, after 100°C. (212°F.) is reached, the determined amount of dry sodium chlorite may be added. In the latter case, boiling is continued long enough for the chlorite to be dissolved and equally mixed with the tallow. Sufficient additional chlorine gas is added to complete the reaction of the chlorite. The total chlorine required is not

[13] J. B. Tuttle and E. R. Woodward, *Chem. & Met. Eng., 53,* No. 5, 114–115 (1946).

more than one-third of the weight of the chlorite used and the gas may be added in 40 to 60 min.

Chlorine addition is carried out in the following manner. Two 150-lb. chlorine cylinders are manifolded together and used simultaneously in order to reduce the rate of withdrawal from each to prevent freezing. The cylinders stand on a platform scale and the outlets are connected to a $\frac{1}{4}$-in. brass tee by means of $\frac{3}{8}$-in. copper tubing. From this tee a single copper tube goes to a 200-lb. chlorine gage and then to a second tee from which two lines branch out, one going to each of the two large kettles. However, both kettles are not used simultaneously. A $\frac{1}{4}$-in. threaded Hastelloy nipple is welded into each tank wall near the base of the cone. A $\frac{1}{4}$-in. Lunkenheimer needle valve with Hastelloy seat and stem is on this nipple. The valve is kept closed until chlorine pressure shows on the gage. Then the valve is opened and chlorine flows into the water layer at the base of the kettle. When chlorine addition is completed, the chlorine valve at the kettle is closed and the chlorine supply is shut off at its source. Agitation with steam continues for a total of 30 min., after which the bleaching reaction is accomplished. The total bleaching process is carried out in 1.5 hours, which represents best practice. The process is carried out in 0.5 hour elsewhere, but because of the speed with which the activating agent is added there is loss of chlorine dioxide from the top of the kettles. Enough dilute caustic is added to raise the pH of the water layer just above 8.

The actual bleaching effect is accomplished by chlorine dioxide, which originates in the "acid activation" process according to the equation:

$$5NaClO_2 + 2H_2SO_4 \rightarrow 4ClO_2 + 2Na_2SO_4 + 2H_2O + NaCl$$

and in the "chlorine activation" process according to the equation:

$$2NaClO_2 + Cl_2 \rightarrow ClO_2 + 2NaCl$$

The use of ClO_2 for bleaching involves a certain amount of hazard. The National Board of Fire Underwriters (Research Report No. 7, 1949) recommended the following procedure:

"Suitable instructions as to safe operation of unit and chemicals should be posted. Operation of the generator should be supervised by a qualified operator. Safety equipment should be readily available. An operator should be stationed at the instrument panel for regular observation of gauges and meters. These and other precautions, if observed, should result in the safe production of chlorine dioxide."

Thomssen and Kemp[14] describe the bleaching of palm oil with sodium dichromate. The reaction is performed in lead-lined tanks at a temperature of 150–160°F. Concerning bleaching of palm oil in air more will be said

[14] E. G. Thomssen and C. R. Kemp, *Modern Soap Making*, MacNair-Dorland, New York, 1937, p. 30.

when dealing with this important raw material, for which this method is exclusively used.

The dichromate method is not widely used at the present time. It depends on the oxidation reaction:

$$Na_2Cr_2O_7 + 8HCl \rightarrow Cr_2Cl_6 + 2NaCl + 7O$$
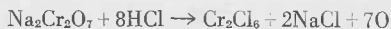
and works best on a low acid clean oil. Approximately 1% dichromate and 2% concentrated hydrochloric acid on the oil weight is required. Half the acid is added to the oil, which should have a temperature between 45 and 50°C. The dichromate is dissolved in the balance of the acid and added slowly to the lead-lined tank of air-agitated oil. After two or three hours, the oil is allowed to settle and the sludge is run off. One or more hot water washes are given to remove the residual traces of chromates and chromic acid.

(B) ADSORPTION BLEACHING

It should be pointed out that in many cases oxidation bleaching of fats and oils, especially with peroxy compounds, may yield products with pale color, but very often color reappears when saponifying these fats and oils in the soap pan. This change is inherent in the nature of oxidation bleaching agents, whose action is generally due to taking up of oxygen. These comparatively labile compounds may subsequently be decomposed during saponification. This, as a matter of fact, is not necessarily the case, but bleaching by the adsorption method is, in any case, free from these drawbacks. The trustworthiness of bleaching by this method of adsorption arises from the circumstance that the coloring matters, mucilaginous substances, etc. are very largely *removed* by the adsorption agent, and not merely modified, as is almost invariably the case in bleaching with oxidizing and reducing agents. This method of bleaching will, therefore, be treated in more detail.[15]

It should first be pointed out that the percentage of bleaching agent varies with the type of oil and the desired bleaching effect. Of course, the quality of the bleaching earth or the bleaching mixture is of decisive influence. This important point is best tested by preliminary experiments. The percentage of bleaching earth or bleaching mixture is generally between $1-5\%$. A good bleaching action depends, first, upon the oil (in cases where it is previously neutralized with lye) being completely free of soap and water, since otherwise a large proportion of the bleaching earth is used up in adsorbing soap, moisture, etc.

Besides, traces of soap impede the action of most bleaching earths, especially the activated earths, by raising the pH of the earth during the bleaching process. In addition, the oil must contain no impurities and as little gummy

[15] J. Davidsohn and A. Davidsohn, *Ind. Chemist, 13*, 281–283 (1937). E. I. Better, *Allgem. Oel u. Fettztg., 29*, 331 (1932).

substances as possible—a condition which applies equally to the unneutralized oil (see XIII, 1). The bleaching is best carried out in a good vacuum, particularly when drying or semi-drying oils such as linseed, hemp, and sunflower are being treated. The use of vacuum is recommended in all cases, since oxidative processes are thus suppressed which otherwise would be detrimental to the effect of the bleaching earth and to the keeping qualities of the bleached oil. Often the reason for chemical changes is sought in the bleaching earth, when they are really due to the occurrence of atmospheric oxidation during the bleaching process. Other causes lie in the oil having been pressed from bad seed, having been expressed at too high a temperature, or having received otherwise unsuitable treatment.

The temperature of bleaching depends on the type of oil and usually ranges between about 110 and 130°C. Various opinions have been expressed by experts as to whether it is best to add all of the bleaching earth in advance or in portions. As it is not likely that the same procedure will be the best for every oil, this point should be investigated experimentally. In vacuum bleaching, the bleaching agent is best added by being drawn into the apparatus by vacuum suction. It must also be pointed out that in vacuum bleaching the bleaching effect itself is not increased, only oxidation processes are precluded. The vacuum vessel must be provided with an efficient agitator, since agitation shortens appreciably the time required for the bleaching. With a good agitator, bleaching time rarely exceeds 30 minutes. It is best to follow the bleaching by withdrawing samples from time to time; these should be run through folded filter papers into a series of similar glasses for comparison of the color measured in a colorimeter. When it has been ascertained that the bleaching is finished, the cooled oil is filtered as rapidly as possible, taking care to avoid excess exposure to air. The oil retained by the bleaching agent must only be blown out by compressed air when the filter press is full, since then only a small proportion of the oil is subjected to possible oxidation. Even here great care is necessary, as will be seen later. If the filter press is not full of spent bleaching agent, it should be left full of oil until filled up with residue from the next bleaching, and then blown. When the bleaching agent is used twice over, e.g., for pretreatment of crude oil, the blowing takes place only at the end of the second bleaching (of the crude oil). Naturally, oxidation of the crude bleached oil is less important, as this has still to be refined and further bleached. As in working with oxidizing oils, the careful refiner will in any case return the blown-out oil to the crudes.

Air blowing of highly oxidizable oils, e.g., linseed or sunflower oil, must be performed with great care, since too strong a blowing may lead to spontaneous combustion or to the cloths being spoiled and recovery of the oil residues being rendered difficult because of the far-reaching oxidation which has taken place—quite apart from the detrimental effect on the quality of the

recovered oil. If it is desired to regenerate the bleaching earth, special pre-
cautions have to be taken with the blowing process, for regeneration of the
earth is very easily upset. Blowing out of the filter presses with steam ensures
maximum recovery of oil. If care is taken to cut off the air or steam supply
when the oil ceases to run from the press, damage to the cloths is practically
precluded. However, the press must be opened immediately after the blowing,
as it is quite possible to burn the cloths, *e.g.*, with soybean or linseed oil.
Further, the spent and blown earth must be removed immediately from the
refinery and spread out to cool. This is especially necessary with soybean
oil, the oxidation of which is so strongly exothermic that it may burst into
flame.

(a) Use of Active Carbon

It has been found that in the bleaching of certain oils a particularly good
effect is obtained by the addition of active charcoal to the bleaching earth.
This applies especially when the finished oil is required to be very pale, and
when the crude oils themselves are very light in color (*e.g.*, coconut and palm
kernel oils). In such cases, a considerable percentage of charcoal is used
(on the bleaching earth); indeed, some plants operate with active carbon
alone, in the proportion of 0.5–1.0% on the oil. This is often done to bleach
coconut oil. The use of active carbon mixed with bleaching earth is nearly
always to be recommended. Carbon alone would not only be too costly in
the majority of cases, but would actually be unsuitable, a better effect being
obtainable with a carbon-bleaching earth mixture, or even with a good bleach-
ing earth alone. Active carbon is thus a valuable adjunct to a bleaching
earth. It is usually used in the proportion of 1 part of charcoal to 8 parts of
earth. The type of active carbon most widely used in the oil and fat industry
is mainly produced by activating charcoals derived from wood or other cel-
lulosic materials such as waste material from the pulp and paper industry.
Bone char is seldom used for bleaching oils and fats.

(b) Use of Sulfuric Acid in Conjunction with Bleaching Earth

Many oils can be bleached by treatment with sulfuric acid and bleaching
earth together. Thus, we have found repeatedly that certain dark liver oils
could be bleached only by treating them first with concentrated sulfuric acid
and then, without removing the acid, by adding bleaching earth. The latter
takes up the acid, so that the acid value of the oils is scarcely increased by
the combined treatment. Generally, 2–3% of sulfuric acid is added very
slowly to the agitated oil at 30 to 40°C., stirring then being continued
for about half an hour. The earth (3–5% on the oil) is then added, and the
whole is gradually warmed to 100°C. The progress of the treatment must be
followed by frequent sampling, particular attention being paid to the acid

value. In the above case, the acid treatment tends to remove albuminous matter present in poorly rendered tallow and produces a product of much greater stability than would otherwise be possible with earth bleaching alone.

DEODORIZATION

This chapter on oil and fat refining may be concluded with a discussion of the process of deodorization. *Deodorization*—the removal of volatile odorous substances from oil and fats—is especially important for the production of edible oils, but it has a certain importance for soap oils as well. Deodorization of oils and fats involves a treatment of the oil by superheated steam in a high vacuum. In effect, deodorization is a form of steam distillation that removes from the oil those constituents which are volatile under the imposed conditions of high vacuum and temperature.[16]

Depending on the character of the oil the percentage of volatile odoriferous constituents varies. It even varies in the same kind of oil. Usually the percentage is very low—from 0.1 to 0.5%. Thurmann[17] summarizes the losses by deodorization at approximately 0.12% in peanut and cottonseed oils and up to 1.75% in beef tallow. However, these losses do not arise exclusively from the odor-producing constituents. They represent also the loss of other volatiles in the oil. The volatile constituents which are eliminated in deodorization vary in the different kinds of oil. Some oils contain bodies belonging to the terpene group; others contain ketones, alcohols, and aldehydes. In rape and similar oils the odoriferous constituents are sulfur compounds, and in fish oils they are nitrogenous compounds. The varying flavors and odors encountered in different crude oils are partly due to the presence of mixtures of the above-mentioned volatile constituents. The characteristic odor of hydrogenated oil is probably due to the reduction products of the ketones and aldehydes.

In a sense, the steam-deodorizing process has a certain similarity to the removal of free fatty acids by means of steam (steam refining). In deodorizing, the percentage of free fatty acids usually decreases, since they are considerably more volatile than the glycerides. There are two methods of steam deodorizing: the batch process and the continuous process. In both, a high vacuum is maintained and superheated steam is injected. In the usual batch deodorizer, the time for complete deodorization varies between 6 and 12 hours. Deodorization time for soap oils may be appreciably lower. Some deodorization plants work in a circulation system. The oil circulates rapidly through a heater, steam being injected into the oil at the entrance into the heater and passes together with the oil through the heating coils.

In the continuous deodorization process only a small amount of oil at a

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[16] J. Davidsohn and A. Davidsohn, *Food Ind.*, 16, 92 (Sept., 1944).
[17] B. H. Thurmann, *Ind. Eng. Chem.*, 15, 395 (1928).

time passes under high vacuum through the deodorizing tower where oil comes into contact with superheated steam. Thus, only a small amount of oil comes into contact with a relatively large amount of superheated steam under vacuum and an optimal effect is gained. The deodorizing tower is constructed similarly to the "bubble cap tower" used in petroleum refining. Superheated steam is admitted at the bottom and it leaves laden with the odoriferous substances at the top.[18]

In conclusion, it should be pointed out that it is very often possible to deodorize oils and fats for use as fat stock for the soap industry simply by blowing steam through it in the soap pan itself or by boiling it over a 5% brine solution. With this simple method it was found possible to deodorize lower grade tallow in a very satisfactory manner.

[18] D. K. Dean and E. H. Chapin, *Oil & Soap, 15,* 200–202 (1938).
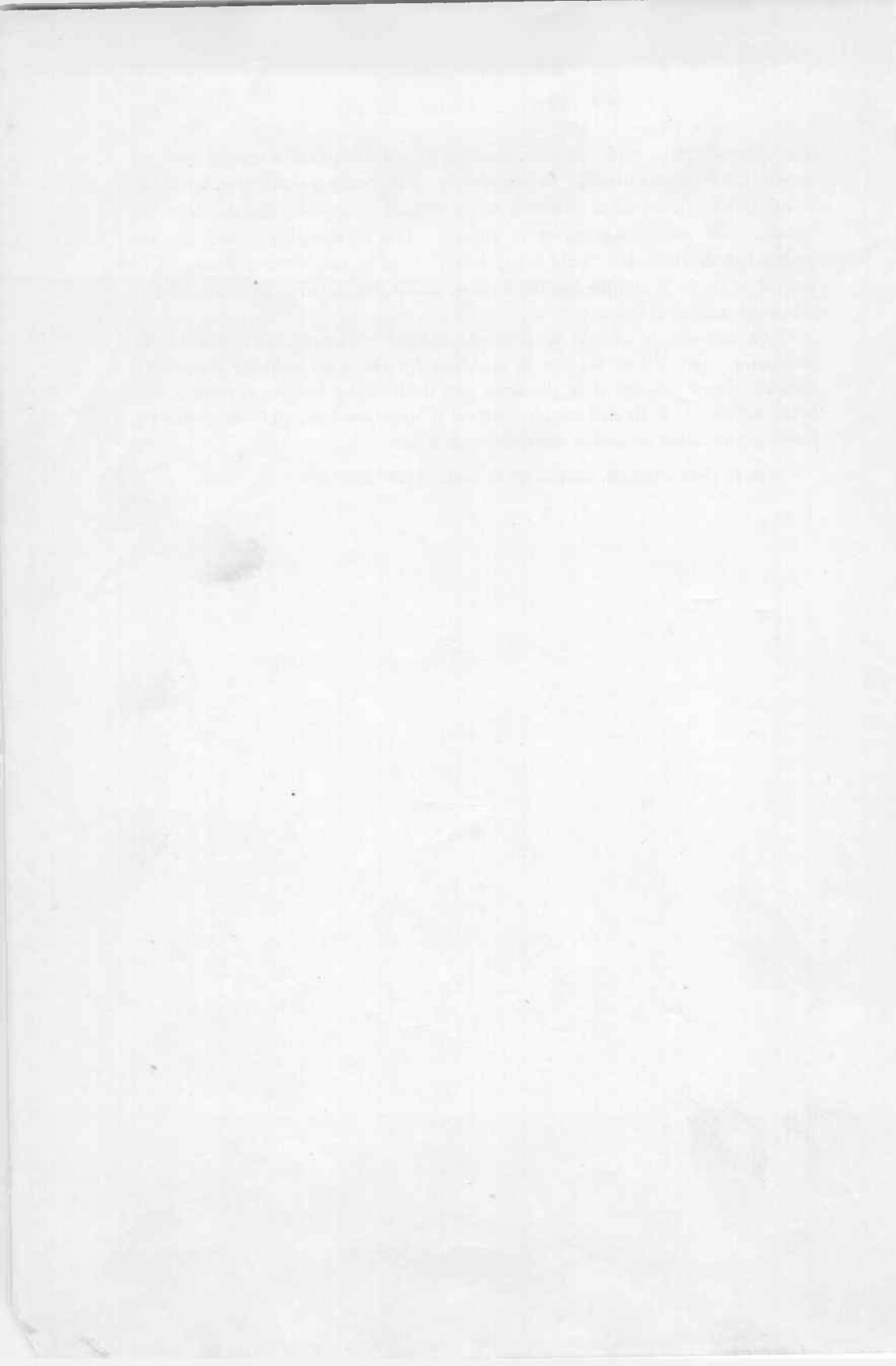
HARDENING OF OILS

The process of oil hardening consists of an addition of hydrogen to the molecule of the oil or liquid fatty acid, and all efforts toward practical realization have been based on this. The addition of hydrogen to liquid fatty acids, free or bound to glycerine as the natural triglycerides, takes place at the ethylenic linkages. From 2 to as many as 6 or more atoms of hydrogen can be introduced, depending on the degree of unsaturation. A typical example, that of the conversion of oleic acid into stearic acid, is as follows:

$$CH_3 \cdot (CH_2)_7 \cdot CH : CH(CH_2)_7 \cdot COOH + H_2 \rightarrow CH_3 \cdot (CH_2)_7 \cdot CH_2 \cdot CH_2(CH_2)_7 \cdot COOH$$
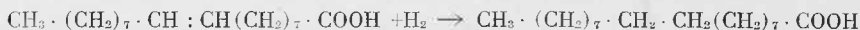
The natural vegetable oils, which are those most concerned in the hardening process, are, of course, mixtures of various unsaturated fatty acid triglycerides. The technical development of fat hardening was based on the Normann process[19] and on a series of other patents on the hydrogenation of oils. In principle, there now exist three methods of fat hardening, distinguished by the method of securing adequate contact of hydrogen, oil, and catalyst.[20]

(1) *The agitation process* (Normann), in which mechanical agitation is used to produce an intimate mixing of nickel, fatty oil, and hydrogen.

(2) *The injection or circulation process* (Testrup,[21] Wilbuschewitsch[22]), in which the mixture of oil and catalyst is withdrawn from the lower part of the reaction chamber and injected as a fine spray into the gas space at the top of the chamber by means of a circulatory pump.

[19] German Pat. 141,029 (1902). Brit. Pat. 1,515 (1903).

[20] T. P. Hilditch, *Industrial Fats and Waxes.* 2nd ed., Baillière, Tindall & Cox London, 1931, pp. 245, 247.

[21] Brit. Pat. 7,726 (1910).

[22] U. S. Pat. 1,024,758.

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(3) The continuous process (Bolton and Lush), in which a special stationary catalyst is employed and the oil passes downward over it and meets an upward current of hydrogen.

As to the mechanism of catalysis, the modern view is that the hydrogen does not first attach itself to the oil, but that unstable complexes are formed on the surface of the catalyst. There, according to Armstrong and Hilditch,[22a] a hydrogen-nickel complex is formed with the unsaturated fatty acids and from this step the stable end product, the saturated linkage in the oil, is formed. It is because the effect is on the surface that it is so sensitive to the poisoning effects of very small quantities of impurities. The inactivation of the catalyst can be brought about in several ways. Long storage may result in reduced effectiveness by oxidation or absorption of moisture. In the hydrogenation itself the catalyst may become poisoned by impurities in the hydrogen or the oil. Carbon monoxide, halogens, and sulfur compounds are typical catalyst poisons which may be found in the hydrogen. It has been stated that the injurious effect of carbon monoxide is reduced by working at high temperatures. In circulatory hydrogenation systems, carbon monoxide may accumulate as the hydrogen is consumed. In this connection, Normann reported on the formation of nickel carbonyl. The bad effects of organic impurities in the oils have been mentioned repeatedly in the literature. The impurities concerned are traces of alkali and sulfur and nitrogen derivatives, mucilaginous and albuminoid compounds, and resins. Refining for hardening includes a treatment with activated bleaching earths, which both bleach and take up mucilaginous matter (see above).

The catalysts used in the two-batch hydrogenation processes are mainly built on nickel, usually by controlled reduction of nickel oxides, carbonate, or formate. Usually the catalyst is mounted on a suitable support to increase its surface and to enhance its even distribution during the process. Various materials have been suggested as supports for the nickel catalyst, including powdered pumice, powdered asbestos, powdered porous firebrick, kieselguhr, china clay, dried silica gels, and numerous varieties of charcoal. The most commonly employed support is undoubtedly kieselguhr.

(1) The Bamag Process

In the Bamag hydrogenation process—built on the agitation principle—only 0.05–0.1% nickel calculated on the weight of oil is necessary. The nickel formate, as used by Bamag, undergoes a thermal decomposition at temperatures of 170–240°C. and a complete reaction is achieved by main-

[22a] E. F. Armstrong and T. P. Hilditch, *Proc. Roy. Soc. London, A98*, 27–40 (1920). For a detailed description of hydrogenation theory see A. E. Bailey, *Industrial Oil and Fat Products,* 2nd ed., Interscience, New York, 1951, pp. 675–678.

taining the maximum temperature in the reduction vessel at 240°C. for approximately one hour. The decomposition equation is:

$$Ni(OOCH)_2 \cdot 2H_2O = Ni + 2CO_2 + H_2 + 2H_2O$$
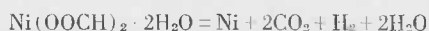
As seen from the above, the reduction does not depend upon the hydrogen action as in the case of the "dry" method. In contrast to this method, where the catalyst is reduced without oil, the catalyst in the "wet" method is reduced within part of the oil to be hardened. Although nickel formate is transformed into nickel without hydrogen, it may still be of advantage to pass a small amount through the reaction mixture during the transformation.

The oil is heated to an appropriate hardening temperature, the specially prepared catalyst is added, and hydrogen is then passed through the hardening autoclave. In practice, a number of important conditions influence the success of the operation, such as purity of the oil, purity of the hydrogen, humidity of the gas, degree of efficiency and quantity of catalyst used, intensity of agitation, etc. Since the hydrogenation is an exothermic reaction, the initial heating is carefully controlled and usually a temperature of 130 to 160°C. is sufficient for the initiation of the conversion. The regulation of the temperatures has been given special attention in this process, since overheating during the operation would seriously affect the color of the oil and increase the FFA content. The best results from the standpoints of color, rate of hardening, and gas consumption are obtained when the temperature is between the limits of 175 and 195°C., although a temperature of 220°C. may be used when certain marine, animal, and fish oils are being processed; this is done to increase the rate of hardening without unduly affecting the color. Correct control of velocity of reaction temperature and pressure is, however, necessary to produce partially hydrogenated products of the correct consistency. Preferential hydrogenation of the less saturated esters to olein and avoidance of the formation of stearin and another completely saturated esters and of hard isoolein are dependent upon the above conditions and are easily achieved. However, when hardening marine, animal, and fish oils to a low iodine number the principle of selectivity must be sacrificed to obtain a satisfactory rate of hydrogenation by using higher temperatures and pressures. During the operation, the rate of gas absorption decreases as the oil becomes more saturated. Samples are drawn and the progress of the hardening determined by means of refractive index, melting point, and/or iodine value (see Ch. XXXVIII). After the desired melting point has been reached, hydrogen flow is shut off and the temperature is reduced appropriately by means of cooling coils or an outside heat exchanger. By utilizing the heat of reaction through a suitable heat exchanger, saving of approximately 10–12 lbs. of fuel per ton of hard fat can be obtained. The hydrogen is purified of CO_2 in a battery of scrubbers. The separated catalyst, with the addition of a small
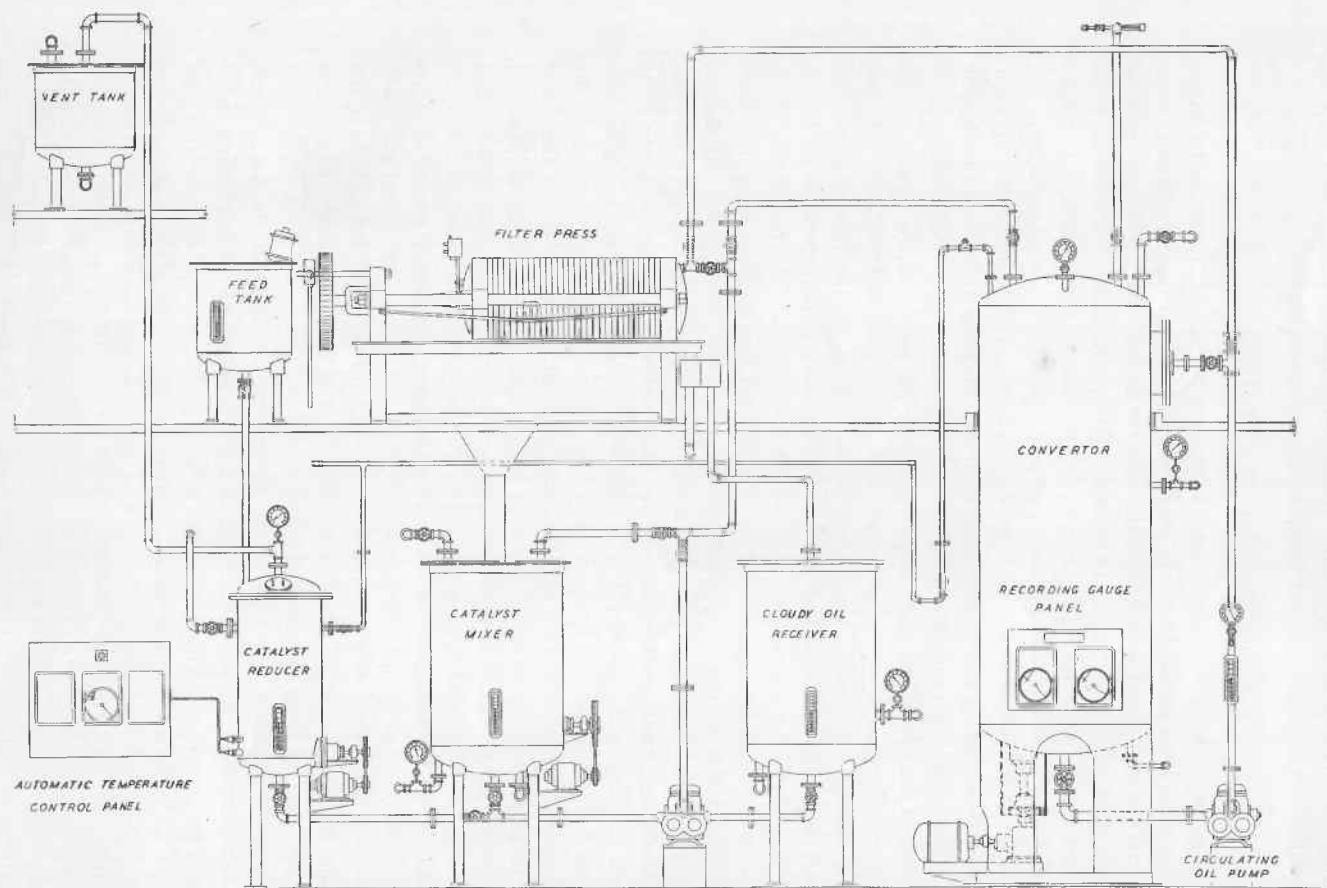
Fig. XIV-1. Oil hydrogenation plant (courtesy Wurster & Sanger, Inc.).[23]

quantity of new catalyst, is used again in subsequent batches of oil until it is no longer sufficiently active to harden a batch in the normal hardening period. Selectivity is not a prime problem in hardening oils for soap use, and hence the reuse of the catalyst is practiced extensively, particularly from edible to inedible use. Usually it is returned for nickel recovery after six or seven passes.

(2) Injection or Circulation Process

The oil to be hardened is mixed with the nickel catalyst and sprayed into a convertor, where the hydrogenation operation is carried out at temperatures of 177–218°C.[23] Here hydrogen is blown into the charge through a spray nozzle. The catalyst and the oil are then circulated back into the convertor by withdrawing them from the bottom. The gas pressure is built up to about 40–60 p.s.i. With new catalyst-refined oil, the gas is absorbed rapidly and the hardening may be completed in 30 to 45 minutes. In large installations five to eight hours are usually allowed for one complete cycle, three to five batches being run per day. For complete hardening of unrefined or partially refined fats and oils in large batches, twelve hours are usually allowed for one cycle, two charges being run per day. Since the reaction is exothermic, it may be necessary to cool the oil during hardening if the temperature rises above the desired limit. This cooling may be accomplished by a cold water coil inside of the convertor, or by circulating the charge through an external heat exchanger and returning it to the convertor through the spray nozzles (Fig. XIV-1). The charge temperature is controlled in this manner. The convertor may be vented and vacuum-pulled once or twice during a run if necessary to remove moisture and inert gases accumulating from the use of impure hydrogen. The time necessary to complete the hardening varies from 20 minutes to 8 hours and depends upon the following factors: (1) activity and amount of catalyst; (2) purity of the hydrogen; (3) character of oil or fat, whether crude, refined, or semirefined; (4) type of oil or fat, whether cotton oil, fish oil, etc.; (5) hardness desired; (6) temperature and pressure used; (7) thoroughness of the mixing; and (8) size of the charge.

The degree of hardening is determined from the refractive index, which may be related to iodine value or to titer.

The number of times a catalyst may be reused depends on the oil, its degree of unsaturation, and mainly on the pretreatment. The purity of the hydrogen is also of major importance. The recovery of the catalyst is a separate type of operation and will not be discussed here except to say that the fat is removed by solvent extraction or by burning off in a furnace, converted to the carbonate, and used from that point or converted to the formate with

[23] O. H. Wurster and G. Stockman, *Processing Oils and Fats*, 3rd ed., pp. 23–24, 26–28. Published by Wurster & Sanger Inc., Chicago.

formic acid. Copper is frequently added to lower the reduction temperature of the catalyst.

(3) The Continuous Process

In the continuous Bolton-Lush process, owned by Technical Research Works Ltd., the oil to be hardened is made to flow continuously over a suitable catalyst, which is in such a form as not to be carried away with the oil. The reaction chamber is formed by a series of, say, eight vertical autoclave tubes in which the oil reacts with hydrogen under pressure. The catalyst is prepared by anodic surface oxidation of nickel shavings or thin perforated nickel plates in a 1% aqueous solution of sodium carbonate. The nickel oxide thus formed is then reduced in the reaction tubes by hydrogen at about 300°C. After cooling to the required temperature, the preheated oil (180–200°C.) is made to "drip"over or to "overflow" the catalyst, in which case the catalyst chamber is filled at all times. The hydrogenation temperature is about 200–260°C. and the pressure is about 60 p.s.i. The hydrogen is made to circulate. The catalyst is so supported that it can be lifted out *en masse*. Exhausted catalyst is extracted with solvents and regenerated by oxidation and subsequent reduction. Advantages claimed for this process are: cheaper plant and operating costs; longer catalyst life and recovery *in toto* provided water is excluded; no hydrolytic fission of the oil, so that subsequent deacidification is unnecessary; the hardened oil contains only 1 p.p.m. of nickel; and only the minimum number of operatives are required and continuous control is possible.

(4) The Hydrogen Supply

Generally, the use of commercial hydrogen is economical for hydrogenation. Large soap manufacturers produce their own hydrogen, by electrolysis, by the steam–iron process, or by propane decomposition.

Three molecules of hydrogen are required to convert one molecule of olein into stearin. Expressed in terms of weight, 0.68% of hydrogen is necessary for such a conversion. The weight of 1,000 cubic feet of H_2 at 760 mm. pressure and at 0°C. (32°F.) is 5.6 lbs. and at 20°C. (68°F.), 5.23 lbs. Therefore, 1 lb. of oil aborbs 0.015 cubic feet or H_2 per 1 unit reduction in iodine value; or 30 cubic feet of H_2 per 2,000 lbs. of oil. With a high quality of electrolytic hydrogen, the actual gas consumption is usually 105–110% of the theoretical, and with less pure hydrogen it is up to 120%.

The hydrogen is usually obtained by the steam–iron process, or by the electrolytic decomposition of water. In some localities hydrogen can be purchased in cylinders at a cost permitting its use for hydrogenation. The use of cracked ammonia and hydrocarbons[24] has been developed and been found practical under some conditions.

[24] The Girdler Hydrocarbon Steam Process, Girdler Corporation, Louisville 1, Kentucky.

Commercial hydrogen contains impurities which may be divided into three groups, in accordance with their behavior during hydrogenation:

(1) Gases which have no effect on the catalyst or the oil. Their effect is merely to dilute the hydrogen. Typical example: nitrogen.

(2) Gases which, under the influence of the catalyst, undergo chemical reactions and thereby use some of the catalyst for such reactions. Typical examples: carbon monoxide, hydrogen sulfide.

(3) Gases or vapors which can react chemically with the oil. Typical example: steam.

Gas made by the electrolytic processes will contain only oxygen and nitrogen as impurities and will run from 99.5 to 99.8% hydrogen. An analysis of such a gas is as follows:

Hydrogen	99.75%
Nitrogen	0.20
Oxygen	0.05

Gas made by the steam–iron process will contain carbon dioxide, carbon monoxide, and nitrogen as impurities, and should contain 98 to 99.5% hydrogen and not over 0.1% carbon monoxide. There must be no sulfur dioxide, hydrogen sulfide, or carbon disulfide in the gas. Sulfur compounds and carbon monoxide act as catalyst poisons. Inert gases such as carbon dioxide and nitrogen act as diluents and decrease the reaction velocity. An analysis of hydrogen made by the steam–iron process is as follows:

Hydrogen	99.1%
Carbon dioxide	0.2
Carbon monoxide	0.1
Nitrogen	0.6

Table XIV-1 from a Bamag publication gives the approximate consumption of hydrogen for different oils, allowing a hydrogen loss of 10%. Table XIV-2 gives the approximate melting points of oils hydrogenated to a maximum point of saturation.[25]

(5) Special Factors in Fat Hardening

Two factors are important for the hydrogenation process:

(a) *The selective nature* of hydrogenation by which, for instance, linolein in a mixture with olein is first transferred into olein before any of the olein originally present is transformed into stearin. This means that any oil (*e.g.*, cottonseed, linseed, soybean, whale oil) is hydrogenated so that all glycerides less saturated than olein (or monoethylenic glycerides) are transformed to the latter before any material increase in the glycerides of the saturated fatty acids occurs. This factor is never achieved in practice, of course, but

[25] T. P. Hilditch, *Industrial Fats and Waxes*, 3rd ed., Baillière, Tindall & Cox, London, 1949, p. 280.

TABLE XIV-1

CONSUMPTION OF HYDROGEN

Oil	Approx. m.p., °C.	Approx. H₂ consumption in cu. ft./ ton, allowing loss of 10%[a]
Coconut	30–32	270
Palm kernel	30–32	380
	38–40	560
Ground nut	30–32	750
	34–36	950
	40–42	1100
	44–46	1500
Soybean	40–42	2450
Sunflower	40–42	2200
Cottonseed	30–32	950
	32–34	1150
	34–36	1450
	40–42	2000
Whale	40–42	2800
	46–48	3350
Castor	83–85	2950

[a] These figures are naturally only to be considered as indicative, since the actual consumption of hydrogen depends on the iodine value of the original oil, which varies within certain limits and operational conditions.

is controlled to some slight extent by conditions of hydrogenation. It is not an important factor in preparing oils for soap use.

On the other hand, over the range of products in ordinary technical use, and for the oils mainly employed in hydrogenation (*i.e.*, whale, fish, linseed, soybean, cottonseed, etc.) the consistency and melting point of the hardened fats may be correlated approximately with their degree of unsaturation (Table XIV-3).

(*b*) The second factor is that during hydrogenation the unsaturated oleic acid may undergo changes such as isomerization without being hydrogenized.

TABLE XIV-2

Completely hydrogenated	Mp., °C.
Coconut oil	43–45
Palm kernel oil	43–45
Herring oil, cod oil	52–55
Whale oil	54–56
Palm oil	56–58
Cottonseed oil	62–63
Olive oil, groundnut oil	68–69
Soybean oil, linseed oil	69–71
Castor oil	86–90

Oleic acid may form isooleic acid, which has a melting point of 45°C., in contrast to normal oleic acid with m.p. 19°C. This of course affects the melting point of the glycerides as well. It is beyond the scope of this book to go further into this matter.[26] However, as for selection, this point has no

TABLE XIV-3

Iodine value of hardened oils		Consistency
80–90	....	Semiliquid, thin pastes
65–80	....	Soft pastes, m.p. 30–35°C.
50–65	....	Soft tallows, m.p. 35–45°C.
35–50	....	Hard tallows, m.p. 45–52°C.
20–35	....	Very hard tallows, m.p. 52–55°C.

great significance to the soapmaker unless the oil is hydrogenated under unusually unfavorable circumstances.

[26] See: T. P. Hilditch, *Industrial Fats and Waxes*, 3rd ed., Baillière, Tindall & Cox, London, 1949, pp. 262–288. A. E. Bailey, *Industrial Oil and Fat Products*, 2nd ed., Interscience, New York, 1951, p. 795 ff. H. K. Dean, *Utilization of Fats*, Chemical Pub. Co., Brooklyn, N. Y., 1938, pp. 121–133.
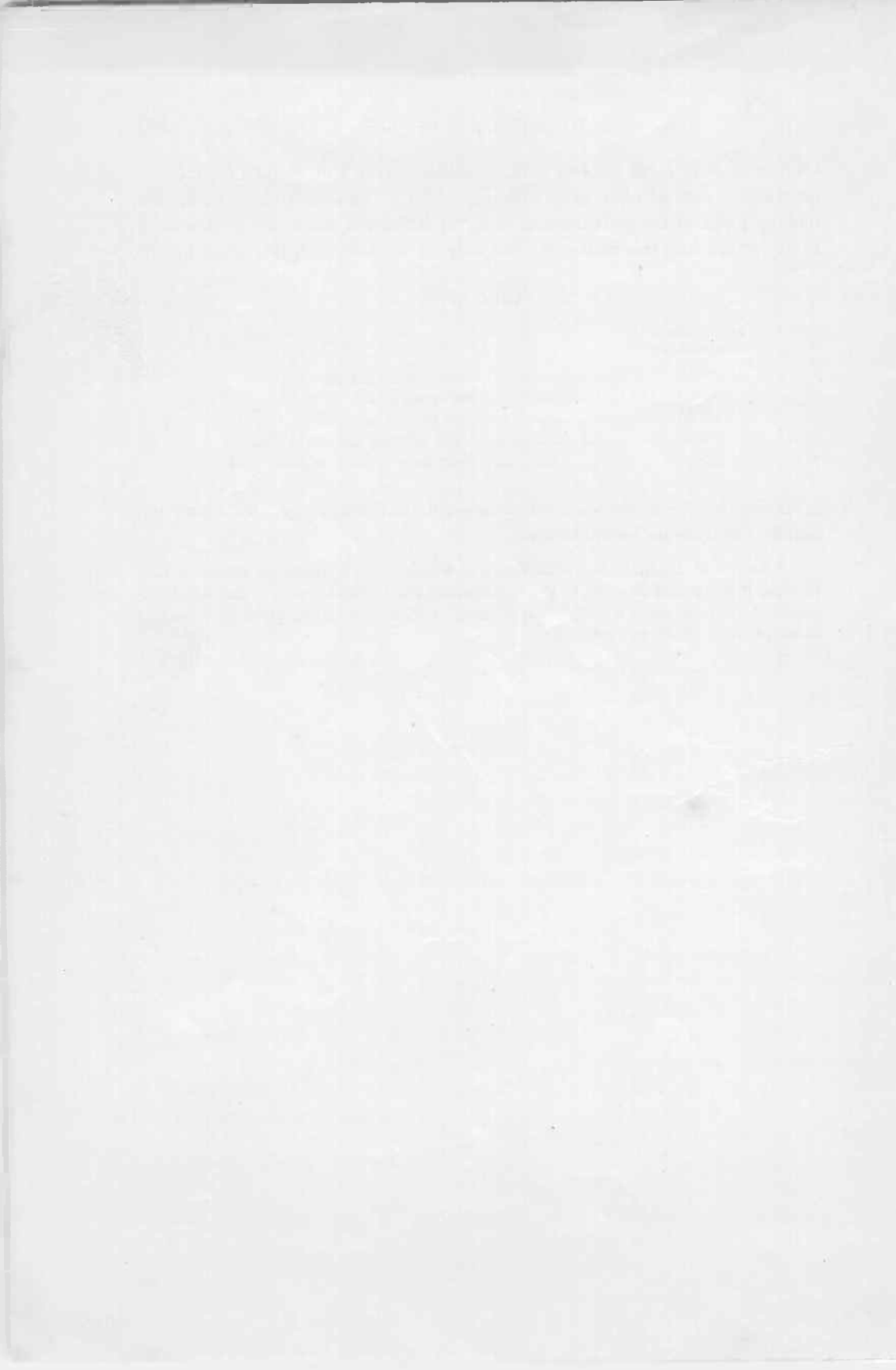
FATTY ACIDS AND THEIR MANUFACTURE

More and more fatty acids are finding their way into the soap pan, replacing neutral fats and oils to a large extent. The war, especially, has speeded up this trend since glycerine became a priority product. Recovery of glycerine by splitting of fats and oils is technically of advantage for the soapmaker. It is more effective than the recovery of glycerine from spent lyes. Besides, fatty acids are easily saponified, even with sodium carbonate, and are especially suited for fast and continuous soapmaking processes. The process of saponification of fatty acids is strongly exothermic and it is thus possible to economize on steam consumption.

As already explained, the splitting of fats is a hydrolytic process at which fatty acids and glycerine are formed by the action of water. The over-all reaction in fat hydrolysis or fat splitting is as follows:

$$
\begin{array}{cccc}
H & & H & \\
| & & | & \\
H-C-OOCR_1 & & H-C-OH & HOOCR_1 \\
| & & | & \\
H-C-OOCR_2 & + 3H_2O \rightarrow & H-C-OH & + HOOCR_2 \\
| & & | & \\
H-C-OOCR_3 & & H-C-OH & HOOCR_3 \\
| & & | & \\
H & & H & \\
\text{Triglyceride} & & \text{Glycerine} & \text{Free fatty acids}
\end{array}
$$
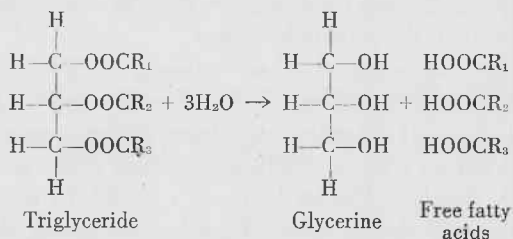
Naturally, the sum of fatty acids and glycerine is greater than 100% of the fat (*i.e.*, 106%) if a neutral fat is completely split. 100 parts neutral fat (with fatty acids of a molecular weight of about 280) give 95 parts fatty acid and 11 parts glycerine. Fats composed of fatty acids of lower molecular weight, *e.g.*, coconut oil, give a higher yield of glycerine. Of course, if

the fat to be split has an acid value, the result will be somewhat less than 106%, since less glycerine will be formed.

The splitting process proceeds in stages, with the fatty acid radicals being displaced from the triglyceride molecule one at a time, so that an incompletely split fat contains both mono- and diglycerides, as well as triglycerides. The amount of mono- and diglycerides is dependent on the method and condition of the splitting process.

(1) The Fat-Splitting Processes

The splitting process may be carried out with or without the aid of catalysts in autoclaves or with the aid of catalysts in open kettles. The first process may be a continuous one, and such a continuous pressure-splitting process is especially suited for the production of fatty acids on a large scale.

(A) Splitting without Pressure

There are three methods of fat splitting in open kettles: (*a*) the enzymic fat-splitting process; (*b*) the sulfuric acid-splitting process; and (*c*) the modified sulfuric acid-splitting process with catalysts.

(*a*) The enzymic process was introduced by Cunnskin, Hoyer, and Waterberg via German patents 145,413 and 188,429 at the beginning of the twentieth century in the course of their research, when they found that oil seeds, especially castor beans, showed a fat-splitting effect in the presence of water. On this basis the process of enzymic splitting was developed. The enzyme preparation is usually obtained from castor beans. The beans are ground with water, and the ground mass is centrifuged to remove solid material. The resulting material, consisting of water, oil, protein, etc., is then fermented at room temperature for 48 hours, after which it is ready for use. The composition of such an emulsion containing the fat-splitting enzyme lipase may have the following composition: 38% castor oil fatty acids, 4% proteinic substance, and the remainder water.

As the splitting temperature has an optimum at 35°C., the process is mainly suited for the splitting of liquid oils. The fatty acids obtained have a light color, which is one of the main advantages of this process. Schlenker[27] describes this process as follows. Splitting is carried out in open, conical-bottomed, lead-lined tanks. The fat is mixed with 30–40% of its weight of water, and about 6% of the ferment. To bring the *p*H of the system to a value of about 5, sufficient acetic or other acid is added, and also manganese sulfate solution equivalent to 0.15–0.20% of the dry salt on the basis of the fat. A temperature of 35°C. is considered optimum, although reasonably

[27] E. Schlenker in G. Hefter and H. Schönfeld, *Chemie und Technologie der Fette und Fettprodukte.* 2nd ed., Vol. II, Springer, Berlin, 1937.

rapid splitting is obtained at temperatures of as low as 15°C. or as high as 40°C. As already mentioned, a higher temperature destroys or at least hampers the activity of the ferment. The mass in the tank is agitated to form an emulsion, and is then held at the proper temperature for about 24 to 48 hours, with occasional stirring. As in other fat-splitting processes, hydrolysis takes place rapidly at first, and then more slowly, eventually reaching a point of equilibrium. About 90% splitting is said to be practicable.

After splitting has taken place, the emulsion is broken by heat (80–85°C.) and the addition of a little sulfuric acid (0.3–0.5%, 50° Bé), after which the fatty acids may be drawn off and washed in the usual manner.

The advantages of this process are low temperature, an inexpensive plant, and light-colored fatty acids. Unfortunately after splitting is completed and sulfuric acid is added, there are usually three layers in the splitting vessel: fatty acids on the surface, an emulsion as the middle layer, and glycerine–water at the low level. It is important to keep the amount of middle layer as small as possible; it consists of an emulsion of the ferment, fatty acids, and glycerine–water. The emulsion is pumped into a separate vessel where it remains for several days at elevated temperature (about 70°C.). Some glycerine–water is recovered after this time. The fatty acids from the middle layer are recovered by saponification as a soap.

(b) The sulfuric acid splitting-process, without the addition of a catalyst, is seldom used, but as it is of considerable historic interest a brief description will be given here. The fats to be split with sulfuric acid are first pretreated by boiling with water. The fat is then removed from the water, and is dried by treating above 120°. At about 110–120°, 4–5% of the fat as sulfuric acid 66 Bé is added slowly with constant stirring. The process is finished after 20–30 minutes. The fat mixture becomes discolored and even turns black. During this process sulfur dioxide is formed which must be removed through a tube system. By the action of sulfuric acid in the fat a certain amount of fatty sulfonates are formed which act as emulsifier in the second stage of this process: namely, boiling the mixture with water and direct steam for 6–7 hours. After this the steam is shut off and the mass is allowed to settle. The dark fatty acids are drawn off from the lower layer of acid–glycerine–water. The plant equipment must be lead-clad to prevent corrosion.

(c) This process was later modified by the addition of a suitable catalyst. These catalysts, certain sulfonates, are taking the place of the sulfonates formed during the treatment of fats with concentrated sulfuric acid in situ. Therefore, after adding the catalyst and sulfuric acid, the process is in a sense only the second stage of the sulfuric acid process is described, and of course the fatty acids obtained are much lighter in color.

The first process of this kind, that of Twitchell, is still widely used in the United States [U. S. Pat. 601,603 (1898)]. The original Twitchell

reagent was a reaction product of a fatty acid, naphthalene, and/or benzene with concentrated sulfuric acid. In the case of naphthalene, the approximate formula of the sulfonate was $(R) \cdot C_{10}H_6 \cdot (SO_2 \cdot OH)$, where R is the fatty acid radical. Today, the reagents used for this *Kontakt* or fat-splitting process are by-products of the petroleum-refining industry: naphthenic or mahogany soaps which are sulfonates of complex structure. The *Petroff* contact reagent is a by-product in the refining of petroleum oils with fuming sulfuric acid; it is said to consist of the sulfonic acids of hydrocarbons, but probably not of the paraffin series. The *Pfeilring* reagent is prepared by sulfonation of castor oil and naphthalene. The *Idrapid* saponifier is probably octahydroanthracene sulfonic acid, and *Nekal BX* is reported to be 1-isopropylnaphthalene 2-sulfonic acid. The effect of these reagents is due to their action as emulsifiers which lower the interfacial tension between the fat and aqueous phases, thereby producing a large oil–water interface at which the hydrolysis may occur besides the hydrolysis which occurs when small amounts of water are actually dissolved in the fat. In this Twitchell, or "Kontakt," splitting process the oil or fat is given a preliminary wash with sulfuric acid and is then hydrolyzed by boiling with sulfuric acid and the special catalyst.[28] Of course, the reaction is a reversible one and consequently a compromise has to be made between the completeness of hydrolysis at the end of the reaction and the final concentration of glycerol in the sweetwater, because as the former increases the latter must be decreased. The usual procedure is to arrange the conditions so that the free fatty acid content of the oil is about 85% after boiling for 12 hours and the glycerol content of the sweetwater is approximately 12.5%. This sweetwater is then run to treatment and the 85% free fatty acid oil is further hydrolyzed to about 95% free fatty acid by a second boil with fresh water. The efficiency of glycerol recovery is improved by using the sweetwater from the second boil for the first boil of the succeeding split.

Thus we see that the process is usually carried out in three stages: (*1*) pretreatment; (*2*) first boil; and (*3*) second boil.

Pretreatment is usually of advantage, since any mucilaginous protein substance has a poisoning effect on the catalyst. It may be carried out as follows. Either the fat is boiled with diluted sulfuric acid or 0.50–2.5% sulfuric acid (60° Bé) is stirred into the heated fat (50–60°C.). The heating and stirring may be carried out with open steam, the steam condensate acting as a diluent for the acid. After 30–60 minutes of stirring, the fat is left standing overnight. In some cases, *e.g.*, linseed oil, the oil is pretreated with 2–3% sulfuric acid of about 77% without application of heat, and afterward it is separated from the dark sludge that settles on the bottom of the vessel.[29] (See Table XV-1.)

[28] J. L. Boyle, *Manuf. Chem.*, *14*, 89–90 (1943).
[29] R. Rosenbusch, *Paint Tech.*, *10*, 281 (1945).

After pretreatment, the splitting proper starts. The amount of catalyst depends on its activity. There are special catalysts of which only 0.75–2% is sufficient to be effective, but some catalysts, *e.g.*, the mahogany soaps, have to be added in amounts of 1–5% of the fat. The catalyst is dissolved either before the sulfuric acid and water are added or vice versa, depending on the catalysts used. The amount of 60° Bé sulfuric acid is in most cases the same as the amount of reagent added. Water is added to the extent of 40% of the fat. (The water should be rather soft, since calcium and magnesium salts tend to break the emulsion.) After water and acid have been added to the fat, steam is introduced through a coil, and when the mixture is boiling the splitting reagent is added. The steam heats up the oil to about 100°C., keeps it at this temperature, and also agitates it. After having passed through the mixture, the steam provides a cover on top of the oily layer, protecting the hot fatty acids from oxygen of the air—a very important matter, especially

TABLE XV-1

PRETREATMENT OF DIFFERENT OILS AND FATS

Oil or fat	Temp. before adding H_2SO_4, °C.	Addn. of H_2SO_4, 60° Bé, %	Treatment time, hr.	Sp. gr. of acid water, (approx.), °Bé
Linseed oil	20	1.5–2.5	1	15
Groundnut or sesame oil	30	1–1.5	1	15
Coconut or palm kernel oil	50	1–1.5	1	15
Cottonseed oil	50	2–2.5	1	20
Grease, etc.	50	1–1.5	1	10
Tallow	50	0.5–1.5	1	10

in the case of linseed fatty acids. A cover over tanks is helpful for this purpose, particularly if a little pressure can be built up.

During settling, when no steam passes through the vat, *shadow steam* is introduced through a branch line and blows over the surface of the oily layer. This is of advantage not only when easily oxidized oils such as linseed oil are to be split, but also in case of other oils and tallow. If the splitting is done in two stages, the first splitting is usually interrupted when the free fatty acids content has gone up to about 80–85%, and this is achieved (provided that the oil had been satisfactorily pretreated) within 10–20 hours, according to the amount of water, reagent, and sulfuric acid used. Now, after settling, the sweetwater is drawn off and a new lot of water (*ca.* 20%) is added; however, additional splitting reagent and sulfuric acid are needed only in exceptional cases because what has already been dissolved in the oily layer usually suffices for the second split. Steam is now again passed through the mixture, and after another 8–15 hours a split of at least 95% is achieved. After the first boil the proportion of fatty material to aqueous glycerine solutions should be about 100 : 65.

The following layout for a three-stage splitting plant gives an idea of the required apparatus (Fig. XV-1).

A melting out trough provides for an easy handling of solid fats which are running into a special settling tank to permit the settling out of any sludge, etc. If necessary, the fat stock then undergoes an acid wash in a special wash tank situated above the two saponification tanks. In the first saponification
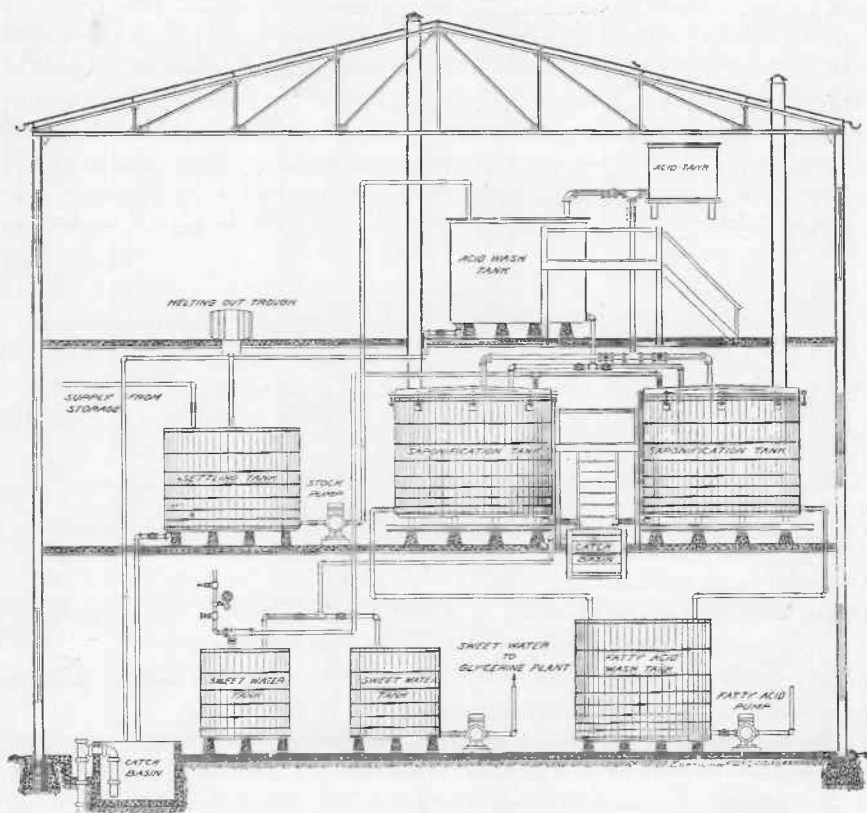
Fig. XV-1. Twitchell fat splitting plant (courtesy Wurster & Sanger, Inc.).

tank splitting is carried out to about 80–85% free fatty acids. In the second saponification tank splitting is brought as near to completion as possible. Two sweetwater tanks provide for the separate reception of the more concentrated sweetwater from the first saponification tank and the less concentrated sweetwater from the second saponification tank. In a separate fatty acid washing tank the fatty acids are washed free from the last traces of mineral acids.

Sometimes a four-stage operation is employed. In this case, three actual splitting operations are made besides one pretreatment stage. The first boil

is interrupted after 60% splitting is reached, the second after an additional 20–25%; and a last third boil for another 10–13% splitting. In this, up to 98% splitting may be reached. The advantage of the Twitchell process is its simplicity; its disadvantages are the rather dark fatty acids and high steam consumption.

(B) SPLITTING UNDER PRESSURE (BATCH PROCESS)

(a) *Introduction.* The autoclave fat-splitting process is actually the oldest such process, the first patent being granted in 1854 to Milly. After the introduction of the Twitchell process the pressure-splitting process suffered a decline. This is understandable as no construction material resistant to the corrosive action of fatty acids at high temperature in the presence of water was available at a reasonable price. Now that this problem has largely been solved by the introduction of stainless steel, the autoclave process has experienced a revival. Fatty acids produced by the autoclave process are light colored and in most cases need not be distilled. It is possible to split fat in an autoclave without the aid of a catalyst at temperatures of 200–220°C. and at pressures around 400 p.s.i. We will see that when splitting fat in a continuous process this method without a catalyst at even higher temperature and much higher pressure has become of great importance. In the common autoclave process, catalysts are used to speed up splitting even at lower temperature and pressure.[30] The catalysts used are of an alkaline character, preferably lime, zinc oxide, or magnesia; zinc oxide is frequently mixed with zinc dust for this purpose in order to improve the color of the fatty acids. The amount of catalyst used varies from 0.5 to 3%. Water is employed in amounts of 40–50% of the oil. With the above-mentioned quantities of catalyst the splitting can be carried out at temperatures of 170–185°C., corresponding to pressures of 110–170 p.s.i. Under these conditions, after 6–8 hours, 85–90% of the fat is split. If a higher split is wanted it is of no practical use to carry on. The hydrolysis of any oil into fatty acids and glycerol is gradually slowed down with the increasing glycerol content of the water because the hydrolysis of the fat is a reversible reaction. Therefore, according to the law of mass action, the hydrolysis of the fat will be slowed down the more glycerol is formed, until the two opposing reactions balance each other. Thus, when the glycerol content of the water has reached a certain amount, say 20%, the first split is broken off at the above-mentioned stage, and the sweetwater—containing the glycerol—is removed under the pressure of the autoclave. Then the whole process is repeated with a fresh amount of water, which by suitable device can be added while the autoclave is still under pressure. After another 2–3 hours a split of nearly 98% is achieved.

[30] R. Rosenbusch, *Paint Tech.*, **10**, 281–282 (1945).

(b) *Effect of Different Catalysts and Other Factors.* The effects of different catalysts was discussed in an extensive research paper published by Lascaray.[31] A small laboratory autoclave was used which was tipped mechanically every other second. The mixture of fat, water, and catalysts was drawn in by suction to the previously evacuated autoclave. The temperature was brought to 185°C. with the apparatus at rest during the course of half an hour. Beef tallow with an acid number of 14, corresponding to a free fatty acid content of 6.8%, was used. Most of the experiments were carried out wtih 0.5% caustic soda which was completely neutralized by the free fatty acids present. The soap formed combined with excess fatty acids to give acid soap, which remained in the fat phase for the most part.

In one series, the temperature was varied from 150 to 220°C. using 60% of water and 0.5% of caustic soda with the fat. The temperatures employed in these tests corresponded to gage pressures of steam as follows: 140°C., 38 pounds; 170°C., 100 pounds; 185°C., 148 pounds; 200°C., 210 pounds; 220°C., 322 pounds. The speed of reaction was increased by an increase in temperature, but the final degree of fat splitting was the same for the upper temperatures, 90–91%. At 220°, this equilibrium condition was reached in 3 hours, at 200° in 5 hours, and at 145° in 8 hours.

In a second series of experiments the percentage of water was varied from 20 to 200%, using 0.5% of caustic soda at 185°C. The speed of the reaction is not influenced by increasing amounts of water, but the final equilibrium is as follows. At the end of 8 hours, 60% of water gave 90% of fat splitting, 100% of water gave 94%, and 200% of water gave 95%. A higher degree of splitting can therefore be brought by an increase in the proportion of water present. The amount of catalyst was varied from 0.25 to 1% of caustic soda. Increase in the amount of catalyst caused an increase in the speed of reaction, although the final state of equilibrium was about the same, the fat being 90.5% split at the end of 8 hours with 0.5% caustic soda and 92.5 with 1% caustic soda. However, the 1% caustic gave about the same degree of splitting at the end of 5 hours as after 8 hours' autoclaving with 0.5%.

The effect of using a number of different alkaline catalysts with 60% water and at a temperature of 185 was studied. Caustic soda, zinc oxide, calcium oxide, magnesium oxide, caustic potash, lithium hydroxide, and ammonia were used in equivalent amounts based on 0.5% of caustic soda. The speed of the reaction was greatly affected by the nature of the catalyst, although the final equilibrium of 90–91% of split fat was reached at the end of 8 hours, except with the use of ammonia and of water alone, when the values were only about 86%. Zinc oxide was by far the most active splitting

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[31] *Fette und Seifen,* 46, 628–632 (1939), through *Soap,* 16, 59–60 (Jan. 1940).

agent, giving nearly the same amount of splitting in 3 hours as in 8 hours. Next came magnesium oxide, then calcium oxide, lithium hydroxide, caustic soda, and caustic potash. Ammonia was not much more effective than water alone. About 2–4% of catalyst is used, based on the weight of the fat, and often a fraction of 1% of zinc dust is also added. The zinc does not act as a catalyst, but, through its reducing action or otherwise, it improves the color of the fatty acids.

In another series, zinc oxide was combined with caustic soda in proportions of 75 : 25, 50 : 50, and 25 : 75, the total corresponding to 0.5% of catalyst. The combinations did not speed up the reaction as much as did zinc oxide alone, but were more effective than would be indicated by the proportionate amounts in the mixtures. The more active catalyst had a greater influence than the less active. For example, the 75 : 25 mixture was nearly as efficient as zinc oxide alone, while the 50 : 50 mixture was better than halfway between zinc oxide and caustic soda.

It has been assumed that catalytic fat splitting is a heterogeneous process taking place at the surface of contact beween fat and water phases. If this were the case, one would expect that reaction would be greatest during the period of greatest emulsification, as the surface of contact is then at a maximum. Under the conditions described above, emulsification is the greatest at the beginning of the reaction when the speed of reaction is relatively slow. As more fatty acids are separated, emulsification becomes less. This was confirmed by actual tests in which fat containing 20% of free fatty acids could be emulsified at 100°C. with water containing 0.5% of caustic soda based on the amount of fat used. With 40% of free fatty acids, mixing was incomplete. With 60% of free fatty acids no emulsion was formed, but fat and water remained completely separated. The speed of reaction is not greatest during maximum emulsification, so that a homogeneous reaction must occur either in the water or in the fat phase, or possibly in both. Experiments described showed that the speed of reaction is independent of the amount of water used. If the reaction occurred in the water phase it would speed up when a greater proportion of water was present. Therefore, the solubility of water in fats and fatty acids appears to be the significant factor.

Commercial fats always contain measurable amounts of water in true solution, not in emulsion form, as shown by the complete clarity of the melted fat. The splitting reaction therefore probably occurs in the fat phase. The acid soaps formed with the alkaline catalyst are soluble in fatty acids. An explanation of the activity of the catalyst lies in its ability to increase the solubility of water in the fat. Direct measurement of the solubility of water in anhydrous fat at 100°C. showed that the water was very much more soluble in fat in the presence of zinc oxide than in its absence.

The period of rapid fat splitting is therefore believed to correspond to the

period of maximum solubility of water in the fat phase. As the reaction approaches equilibrium, the glycerine formed decreases this solubility and the reaction slows down. This new explanation seems to agree with all of the observed facts. After the splitting in the autoclave is finished, the contents of the autoclave, the two layers separately, if desired, are blown over, again under its steam pressure, to an open lead-lined tank, and there the upper layer containing the fatty acids and their Ca, Zn, or Mg soaps is treated with mineral acids in order to decompose these metal soaps. Sulfuric acid is added, and by introduction of a vigorous current of steam the whole is brought to the boil. After some time the acid water containing the metal sulfates and some more glycerol is allowed to settle down and is drawn off. Afterward, the oil layer is washed repeatedly with water and steam as before, until it is entirely free from mineral acid. This is especially important where the fatty acids are to be distilled later on. In this case the presence of mineral acids must be carefully avoided. However, treatment with mineral acid is unnecessary when no catalysts were used. This makes the pressure fat-splitting process especially suited for continuous operation. But before dealing with this most recent development in fat splitting, the common autoclave process with addition of a catalyst shall be described with the help of Fig. XV-2.

(c) *Equipment.* The fats are emptied into a tank and pumped into the the pretreatment and washing tank. Here, in a lead-clad or otherwise acid-resistant tank, the fats may be treated by indirect or direct steam. (In Fig. XV-2 the tank is not fitted with pipes, but according to our experience we would advise steam pipes.) In some cases, simple heating brings the coagulated mucilaginous substances in a foam to the surface, in other cases, addition of sulfuric acid is necessary. In principle the pretreatment is the same as described for the pretreatment of fats for the Twitchell process. The pretreated fat is best left to settle overnight. The reagents are prepared in the measuring tank. All catalysts must be finely ground and pure (especially free from iron).

Now the fat, water, and the catalyst are introduced into the series of autoclaves where the actual splitting is carried out. Either by means of steam injection or mechanical stirring the fat–water–catalyst mixture is strongly agitated to accelerate the splitting process. Samples are taken from time to time from special valves and analyzed (see Ch. XXXVIII). After the splitting result has been found satisfactory, the mixture is blown under its own pressure into the flash chamber. Care must be taken not to blow out at too high temperatures and too fast in order to avoid loss of glycerine. In the water tank, soft water is kept ready as "make-up water." The fatty acids are then introduced into the fatty acids and sweetwater tanks, where they are washed and are pumped from there into storage, the soap pan, or the distilling plant.
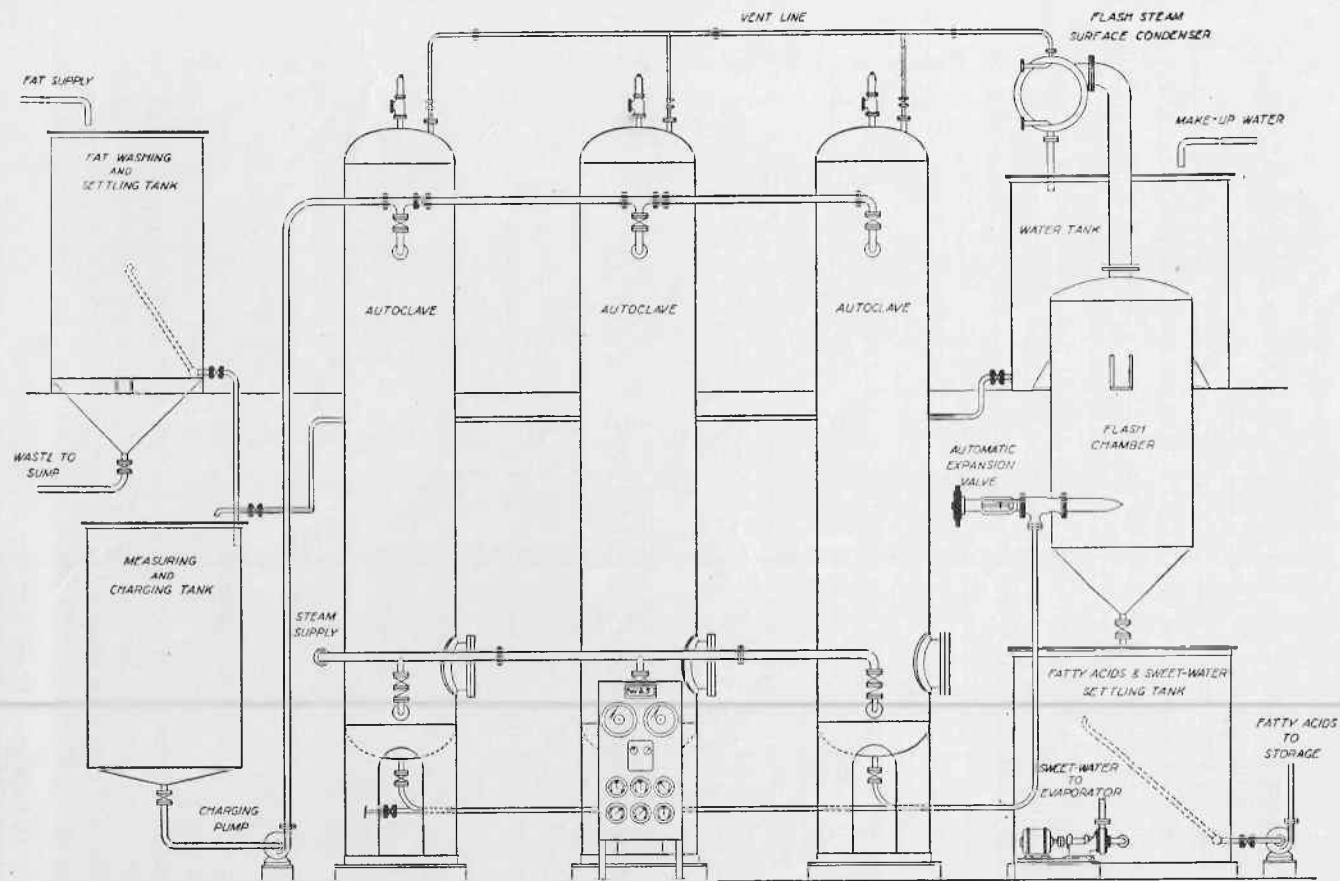
Fig. XV-2. High pressure autoclave fat splitting plant (courtesy Wurster & Sanger, Inc.).

(C) Continuous Pressure Splitting

Wurster[32] in a report on the principles of modern continuous fat splitting, wrote: With the introduction of nickel clad and stainless clad steel, there came a new development in the batch autoclave process. These new materials permitted the construction of stronger and larger autoclaves, and vessels were built for charges of 15,000 to 25,000 lbs. and to be operated at pressures up to 175 p.s.i. A further advance in the autoclave process was made by designing them to operate at steam pressures around 400 p.s.i. The fat is then split without the use of a catalyst. This eliminates subsequent treatment of both the fatty acids and the glycerine sweetwater to remove the catalyst products and effects an appreciable saving in operating costs. Inconel clad steel has also become available as a superior metal of construction for these autoclaves. At the same time that the high pressure autoclave for operation without catalyst came into use, these new materials of construction made it possible to develop continuous processes of fat splitting at high pressure and temperature with and without catalyst.

There are two types of continuous plants in commercial operation, countercurrent and parallel flow. In the countercurrent processes the water is fed in near the top of a vertical reactor vessel, while the fat is fed in near the bottom. The fatty acids then flow countercurrent to the water and out at the top, whereas the water and glycerine are removed at the bottom. The operating conditions are approximately 250°C. and 800 p.s.i.

In the parallel flow processes the fat and water are mixed, the mixture pumped through tubular heaters and discharged to receivers for the subsequent separation of the fatty acids and glycerine sweet water. The temperatures used are around 315°C. and the pressure 3,500 p.s.i.

The continuous fat-splitting method of the Eisenlohr process is described as an example.[33] The fat to be treated is deaerated and then mixed and emulsified with water; the emulsion is pumped at high pressure (3500 p.s.i.) through specially designed coils made of Inconel, in which the temperature is brought up to about 330°C. and the split is effected without the use of catalyst. The pressure is let down through an expansion valve and the fatty acids–sweetwater emulsion is concentrated by passing through a flash chamber. The water vapor evaporated in this vessel is used to evaporate the sweetwater for the production of crude glycerine and the condensate removed from the sweetwater evaporator calandrias is returned for reuse in the fat-splitting process. After concentration, the emulsion is passed through a cooler and then to a settling tank, where the fatty acids and sweetwater are separated. The fatty acids are cleaned and are ready for immediate use.

[32] O. H. Wurster, *Chem. Met. Eng.*, *52*, 220 (May 1945).
[33] The Power Gas Corporation, Stockton-on-Tees, England.

The sweetwater requires no chemical treatment before passing to the evaporators for the recovery of glycerine (see Chapter XXXIV), although it is sometimes filtered to remove any traces of fatty acid.

It will be seen that important cost savings are made in this process by eliminating treatment of both fatty acids and sweetwater and reducing the amount of evaporation required.

TABLE XV-2

130-DAY CORROSION TEST ON STORAGE TANKS CONTAINING MIXED CONCENTRATED
FATTY ACIDS FROM FISH OILS
Temperature 160–260°F.

Material	Inch penetration per year
Monel	0.0018
Nickel	0.0029
Inconel	0.0001
Mild steel	0.0066
Cast iron	0.064

It must be pointed out that many continuous fat-splitting processes are in fact continuous soap manufacturing processes; they are discussed as such in the corresponding chapter of this book. The continuous fat-splitting process is economical where the quantity of fat handled is of the order of 50 tons a day or so.

(D) MATERIALS OF CONSTRUCTION

It was pointed out earlier that the material of construction is of major importance. Stainless steels or Inconel, a chromium nickel alloy (80% Ni, 14% Cr, and 6% Fe) are used for the construction of the high pressure fat-splitting coils. The high corrosion resistance of Inconel is indicated in Table XV-2, which gives the rate of corrosion of fatty acid storage tanks constructed of various metals at an average temperature of 200°F. (93°C.).

Each type of service requires the study of its own particular metal requirements. Corrosion is just one of many factors involved and requires the study of expert engineering advice.

(E) SPLITTING OF SOAPSTOCK

Soapstock from the oil refining plant is another source of fatty acids. The soapstock is split by treatment with dilute sulfuric acid and the fatty acids are skimmed off and washed free of acid. Usually the contents of free fatty acids in these products are relatively low, from 40–70%, the remainder being neutral fat which was absorbed during the refining process. If it is desirable to split this neutral fat as well as the fatty acid, the mixture is sub-

mitted to one of the fat-splitting processes. On occasion, the soap is made from an oil for the sole purpose of obtaining the fatty acids by acidification. In this case the free acids contain relatively little unsaponified matter. An example of this might be the procurement of small quantities of ricinoleic acid from castor oil, etc.

(2) Fatty Acid Distillation

The most effective way of purifying fatty acids is to distil them.[34] The early batch distilling process was carried out in direct-fired pots at about 300°C. in the presence of a current of superheated steam. The distillation was carried out as follows: A large amount of crude fatty acids is heated with direct fire or with hot water in pressure tubes (Frederking system). During the heating process, steam is injected. After some hours the contents of this distilling vessel are only partly distilled. Neutral fat, unsaponifiable materials, color material, and also a considerable part of the fatty acids themselves were left behind in the pitch. Of course, this pitch has a very low market value. Since the crude fatty acids remain for many hours in the distilling vessel, it would be expected that the amount of pitch would be high. Technical improvements aimed to improve the yield and quality of the product were made in three directions. By reducing the pressure in the distillation plant, the temperature could be lowered to about 250°C. With very high vacuum, not exceeding 6 mm., and the use of carefully measured amounts of superheated steam, the temperature may be brought down to 200–210°C. This improved the product and yield by lowering decomposition and polymerization, especially of unsaturated fatty acids.

This also permits the use of indirect heating accomplished, for instance, by circulating hot liquids such as mineral oil at high pressures up to 2000 p.s.i., or by vapors of Dowtherm (a eutectic mixture of diphenyl and diphenyl oxide).

Finally, in order to prevent deterioration of the fatty acids, they should be exposed to the distillation temperatures for as short a time as possible. This can be accomplished most readily by continuous distillation which has not only the advantages inherent to all continuous operations, but yield fatty acids of higher quality and less pitch.

The Wecker system[35] is one of the earliest and most successful of the continuous distillation processes. It is also a steam refining process to remove free fatty acids from crude oils (Ch. XIII, 2). Crude oil or crude fatty acids, e.g., split soapstock fatty acids, is precleaned by passing

[34] J. Davidsohn and A. Davidsohn, *Soap, 15*, No. 8, 21–23, 70 (1939).

[35] German Pat. 397,332. Brit. Pat. 213,267 (1923). U. S. Pat. 1,622,126 (1927).

through several screens which retain most of the impurities suspended in the oil. It is then allowed to flow through an inlet inspection glass into the reaction apparatus in which the separation of the fatty acid from the neutral portion is affected. The reaction apparatus, made of special acid-resisting material rectangular in shape with a number of interconnecting chambers, is heated to a temperature of 200–280°C. to vaporize the fatty acids. The crude oil flows in a thin film along the bottom and the deacidification or distillation takes place. Owing to the high vacuum maintained in the distillation vessel the particles of the relatively cold injected steam expand instantaneously; the consequence of this violent explosion-like evaporation of liquid in oil causes the vaporized fatty acid and all the volatile odorous constituents to leave the vessel in the form of a thick fog at a temperature of 120–150°C. This vapor is then directed into the cooler, where the condensation of the fatty acids and other volatile constituents is affected. It has become possible to distil highly unsaturated fatty acids without decomposition and polymerization; even waste fats of pure quality may be distilled by this method. The process was developed initially to remove free fatty acids from oils and fats instead of having to resort to the conventional alkali refining process, but it is chiefly adapted now to distil the fatty acids themselves or to distil highly acid soap stock fatty acids, leaving the practically unchanged neutral fat behind.

Tolman and Goranflo[36] have described a continuous high vacuum steam distillation process developed from experiences gained in the petroleum industry. It is called a *flash distillation* process. The acids are preheated in the condenser and second preheater and are injected toward the top of a distilling tower fitted with ordinary tray and bubble cap tower, so that intimate contact between steam and fatty acids is obtained. The feed stock and stripping steam is heated by Dowtherm vapor.[37] Dowtherm heating is highly advantageous in comparison with direct firing, since Dowtherm vapors can be condensed at a temperature only slightly above that desired in the feed stock; thus, overheating and polymerization of acids in stagnant films or "dead spots" is avoided (Fig. XV-3). The relative efficiency in yield and residue of the different distillation processes is illustrated by the following figures:[38]

Type of distillation	% yield	% of residue
Batch	85–90	10–15
Continuous	95–97	3–5
Flash	> 97	< 3

[36] L. M. Tolman and S. Goranflo, *Oil & Soap*, 12, 26 (1935).

[37] A. E. Bailey, *Industrial Oil and Fat Products*, 2nd ed., Interscience, New York, 1951, p. 885.

[38] H. G. Kirchenbauer, *Fats and Oils*, Reinhold, New York, 1944, p. 62.

LEGEND

1. DRYER FEED PUMP
2. DRYER-DEAERATOR
3. STILL FEED PUMP
4. STRIPPING STILL
5. FLICK SEPARATOR
6. PRIMARY CONDENSER
7. FINAL CONDENSER
8. VAPOR SCRUBBER-RECEIVER
9. HIGH VACUUM SYSTEM
10. RESIDUE PUMP
11. PRODUCT RECEIVER
12. PRODUCT DISCHARGE PUMP
13. PRODUCT COOLER
14. SCRUBBER PUMP
15. DOWTHERM STORAGE TANK
16. DOWTHERM BOILER
17. BOILER CONTROL PANEL
18. PROCESS CONTROL PANEL
19. STRAINERS

A. CRUDE FATTY ACIDS FEED
B. LIGHT ENDS DISCHARGE
C. PRODUCT DISCHARGE
D. RESIDUE DISCHARGE

Fig. XV-3.   Continuous fatty acid distillation plant (courtesy Wurster & Sanger, Inc.).[38a]

Probably the most efficient and modern method of all is to combine very high vacuum of the order of a few tenths of a millimeter of mercury with the flash evaporation principle and to do away with steam injection altogether. In this case the fatty acids are sprayed directly into the vacuum chamber.

R. W. Berger[38a] describes recent progress based on this line of thought. He summarizes the improvements of such a plant (Fig. XV-3) constructed by Wurster & Sanger, Inc., Chicago, as follows: "In the simple distillation of fatty acids, improved results with respect to product quality, uniformity, and yields are obtained with reduced plant operating and space requirements because of the following factors: (1) Continuous operation under automatic instrument control. (2) Deaerating the feed stock before heating. (3)

[38a] R. W. Berger, *J. Am. Oil Chem. Soc.*, 29, 81–87 (1952).

Vacuum drying the crude fatty acids at low temperatures (at 150–200°F. under a vacuum of 26–28 inches Hg). (4) Indirectly heating the fatty acids to distillation temperatures by means of condensing Dowtherm vapors within the bubble trays of a stripping still. With this unique heating system the fatty acids are not exposed to high temperatures until they are under the high vacuum within the still itself (The maximum operating temperature, when distilling a mixture of fatty acids with a vapor pressure of 5 mm. Hg at 400°F. actually would be about 400°F. The maximum surface temperature to which the fatty acids are exposed during a very short period is in the range of 525–625°F.), thereby eliminating the preheating of feed stocks far above distillation temperatures before they are under high vacuum. (5) Low hold-up and minimum heat transfer surface temperature in the stripping still. (6) Removal of entrainment from the distillate vapor stream before condensing the product. (7) Efficient product condensing system and cooling the product before discharge to the atmosphere. (8) Residues which are easily handled for recovery of free and combined acids. (10) Freedom from metallic contamination, because of all stainless steel construction, wherever contacted by fatty acids."

Another plant based on Dowtherm heating system and also suitable for small scale operation (12 tons daily) is constructed by James P. O'Donnell Engineers, New York. The Dowtherm heated distillation column contains Koch cascade trays, and the fatty acids may be fed at alternate feed locations at different heights of the distillation column. There is a central control panel which records the process variables. In this plant preheating of the fatty acids is done through a coil passing through the top of the distillation column. The whole plant is very compact and may be operated by one man (Fig. XV-4).[38b]

As already pointed out, fatty acids are very corrosive to ordinary carbon steel at high temperatures. A suitable material for the construction of stills is a type 316 or other molybdenum-stabilized stainless steel. Ordinary, 18-8 stainless steel is said to be not much more resistant than ordinary steel. Table XV-3 shows the resistance to corrosion of different material of construction in an actual field test carried out inside a vacuum still for refining crude fatty acids.[39]

Monel has the approximate composition: 68% Ni, 28% Cu and 2% Fe, together with small percentages of Mn, Si, etc. Inconel has the following approximate composition: 80% Ni, 14% Cr, and 6% Fe. Aluminum is also recommended as material of construction for fatty acid production plants and the storage of fatty acids, but it has several drawbacks: its easy deforma-

[38b] *Chem. Engineering, 59,* No. 2, 252, 254 (1952).
[39] "Monel Notes," No. 19 (1945). Henry Wiggins & Co., London.
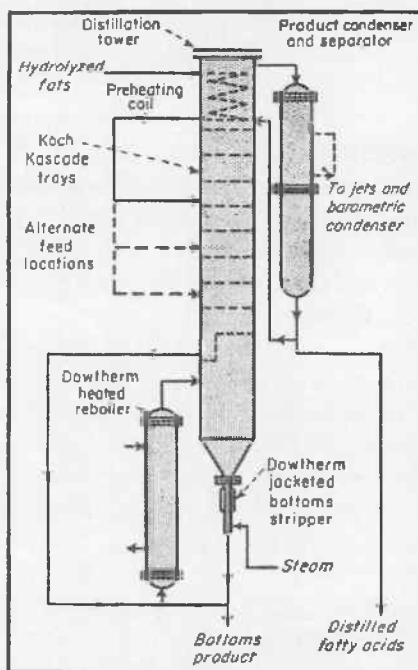
Fig. XV-4. O'Donnell continuous fatty acid distillation plant.[38b]

tion, its lack of alkali resistance, and the special technique required in fabrication. Another step in fatty acid distillation is the fractional distillation of fatty acids.[40] Briefly, the method consists of inserting a fractionating column above the still receptacle. This is frequently of the bubble-cap type and must be strongly resistant to corrosion. Since the separation of fatty acids is proportional to their molecular weights, it is seen readily that oleic (282) cannot be separated from stearic (284), whereas both can be separated to some de-

TABLE XV-3

Metals	Corrosion rate. in. penetration per yr.	
	Vapor	Liquid
Inconel	0.0008	0.0011
Monel	0.0025	0.0039
Nickel	0.0033	0.0041
18-8 stainless steel	0.0016[a]	0.0012[a]
Ni-Resist	0.014	0.015
Cast iron	0.73	0.79

[a] The specimens were pitted with many shallow pits.
40 A. E. Bailey, *loc. cit.*, pp. 887–88.

gree from palmitic (256). The lower saturated acids can be separated even more readily from one another—lauric (200) from myristic (228), etc. For this reason most of the fatty acids for soapmaking are distilled for purposes of purification only and fractionation is reserved for those fatty acids that contain short chains, such as coconut oil, palm kernel oil, etc. By distilling off the low molecular fractions, *i.e.*, caproic, caprylic, and capric acids of coconut oil or palm kernel fatty acids especially purified fatty acids are produced, which do not show the disagreeable "bite," *i.e.*, the skin sensitizing effect which is generally attributed to the soaps of the caproic, caprylic, and capric fatty acids (see Chapter XXXII).

TABLE XV-4

Properties	Lauric acid	Myristic acid
Mol. wt. (nominal)	200.2	228.2
Mol. wt. (mean)	203.0	226.0
Titer	37.8	42.0
Iodine value	1.0	2.0
Acid value	276.0	248.0

Lauric, myristic, caprylic, and capric acids are available in approximately 80–90% purity from this source, while stearic and oleic must be obtained by crystallization or other methods as described later in Section 3. The data on two important soapmaking acids, lauric and myristic, as produced by fractional distillation, is given in Table XV-4.

The physical characteristics of sodium and potassium myristates are those that may be expected from the position of myristic acid between lauric (coconut) acid and palmitic (palm oil) acid. These myristic acid soaps have the quick lather of coconut soaps and the rich creamy suds of higher titer palm oil soaps combined, but without the irritating effect on skin so characteristic of coconut oil soaps; this is due to the presence of fatty acids of low molecular weight (capric, caprylic, etc.) in coconut oil. The high titer, good color, and pleasant odor suggest the use of myristic acid in high quality toilet soaps, shaving creams, and other toilet preparations. The 50% potash soap is a soft soap of excellent detergent value for textile purposes. Ethylenediamine, morpholine and the ethanol amines form light-colored, easy lathering soaps. Triethanolamine gives a light-orange soap if adequate proportions are warmed together (246 parts myristic acid plus 140 parts triethanolamine). The resulting soap, when cool, is a solid, waxlike, yellowish mass, which can be brought to any consistency by the addition of water.

Formulas for shampoos and shaving cream containing myristic acid will be found in the corresponding chapters.

(3) Fractionating Fatty Acids by Crystallization

(A) Stearic Acid and Red Oil

The separation of stearic acid and oleic acid from tallow fatty acids is the oldest commercial process for separating different fatty acids by crystallization. The distilled tallow fatty acids are charged into shallow pans and caused to solidify by bringing down the temperature slowly to about 4–5°C. in refrigerated rooms. The solid cakes are removed from the pans without breaking, are individually wrapped in press cloths, and are subjected to moderate pressure in hydraulic plate presses. The liquid expressed constitutes commercial oleic acid or red oil and contains, besides oleic acid, some dissolved saturated acids, and some linoleic acid. The solid fatty acids in the press cloths are known as "single pressed" stearic acid. These cakes are recast and subjected to heat pressing in specially constructed heated presses. This process may be repeated, thus producing "double" or "triple" pressed stearic acid. The triple pressed product is especially important in the production of shaving creams or sticks. The accompanying figures show the characteristics of different commercial stearic acids.

Characteristics of Some Commercial Stearic Acids

Sample	M. p., °F. (°C.)	Iodine value (av.)	Titer (av.)
Single pressed	125–126 (51.7–52.2)	15	53.2°C.
Double pressed	128–129 (53.3–53.9)	8	54.2°C.
Triple pressed	130–131 (54.4–55.0)	3[a]	55.2°C.

[a] The United States Pharmacopeia prescribes an iodine value below 4 for *Acidum Stearicum.*

Neutralization values of commercial stearic acid are between 200 and 210. Unsaponifiable matter in stearic acids from distilled tallow fatty acids is practically nil; from undistilled tallow fatty acids it may represent up to 1%. Commercial oleic acid or red oil from tallow may have the characteristics shown below:

Sample	Titer	Iodine value	Unsaponifiable	Neutral fat
Undistilled	15–18°C.	78–83	Max. 5%	Max. 10%
Distilled	8–12°C.	90–93	Max. 3%	Max. 3%

The saponification value of commercial oleic acids is normally between 200 and 205.

(B) Fractional Crystallization of Fatty Acids in Solvents

The next development in separation of fatty acids was by crystallization from suitable solvents. By this method, not only tallow fatty acids could be

separated in different fractions, but also the fatty acids from practically all sources. The first commercially effective process was the Emersol process by Emery Industries and constructed by Blaw-Knox.[41] The crystallization is carried out by chilling the distilled fatty acids with the help of a crystal promoter in methyl alcohol. The crystallized fatty acids are filtered from the alcohol solution on an enclosed rotary vacuum filter. In the *oleic still* the methyl alcohol is distilled from the filtrate, and in the *stearic still* the alcohol is removed from the filter cake. The following results were obtained on fatty acids from Twitchell splitting and vacuum distillation:

Tallow (No. 1 tallow). Titer 42.4°C., I.V. (iodine value) 52.2. When treated by the Emersol process yielded:
      Stearic acid. 51%, titer 54.1°C., I.V. 6.0.
      Oleic acid. 49%, titer 2.0°C.
Grease (white grease). Titer 38.7°C., I.V. 62.5. When treated by the Emersol process yielded:
      Stearic acid. 38%, titer 53.7°C., I.V. 6.0.
      Oleic acid. 62%, titer 2.0°C.
Stearine (yellow grease stearine). Titer 45.2°C., I.V. 44.7. When treated by the Emersol process yielded:
      Stearic acid. 52%, titer 54.1°C., I.V. 6.0.
      Oleic acid. 48%, titer 2.0°C.
Garbage grease. Titer 37.5°C., I.V. 68.4. When treated by the Emersol process yielded:
      Stearic acid. 35%, titer 53°C., I.V. 6.0.
      Oleic acid. 65%, titer 2.0°C.
Note that the high titer tallow and high stearine yield a larger quantity of high titer stearic acid than is obtained from the lower titer lower grade fats.

When *vegetable oil* fatty acids are treated by the Emersol process, the solid acid usually obtained is mainly palmitic acid which is particularly suitable for use in the manufacture of cosmetics. Results obtained with palm oil and cottonseed oil are as follows:

Palm oil. Titer 45.0°C., I.V. 52.9. When treated by the Emersol process yielded:
      Solid acids. 55.5%, titer 55.1°C., I. V. 14.0.
      Liquid acids. 44.5%, titer 4.0°C.
The relatively high I.V. of the solid acids (chiefly palmitic acid) is not objectionable in the manufacture of shaving soaps.
Cottonseed oil (cottonseed foots). Titer 35°C., I.V. 98. When treated by the Emersol process yielded:
      Solid acids. 36%, titer 49.5°C., I.V. 32.5.
      Liquid acids. 64%, I.V. 137.

The above described method seldom gives a red oil of greater purity than about 75% oleic acid for two reasons. First, tallow itself contains a few per

[41] Blaw-Knox Bulletin No. 2051. R. E. Kistler, V. J. Muckerheide, and L. D. Meyers, *Oil & Soap*, **23**, 146–150 (1946).

cent of the highly unsaturated linoleic acid which concentrates in the red oil fraction to approximately 13%. The presence of such unsaturated acid tends to solubilize the saturated ones, making them hard to remove. By pretreatment of the tallow or tallow acids by slight hydrogenation before pressing,[42] it is possible to raise the purity of the resulting red oil to above 90% oleic. Treatment to polymerize the linoleic will have a similar effect, although the practical application of this method to tallow is restricted.[43]

To summarize, the separation of fatty acids mixtures into fatty acids of distinct types makes it possible to manufacture "tailor made" soap from acids chosen for the specific properties they give to a soap produced from them.

(4) Advantages of Fatty Acids for Soap Manufacture

The advantages of the use of fatty acids for the soap industry are described in an article by Stingley.[44] He points out that in spite of the fact that according to the last figures of he U. S. Bureau of the Census before the war, only 5% of the fat raw materials for the soap industry were fatty acids (about 100 million pounds out of 2 billion pounds), they are, however, being used more and more in the soap industry in the United States and abroad. The advantages of fatty acids, especially if brought on the market as processed raw material with definite characteristics, allow the production of soap of uniform quality. Fatty acids may be saponified directly in crutchers and need not necessarily be boiled in the soap kettle. Saponification of fatty acids proceeds rapidly, and, because it is a strongly exothermic process, heat consumption is greatly reduced. Since fatty acids saponify in a fraction of the time required for natural oils, crutcher turnover is speeded up, giving increased capacity without additional equipment, thus reducing both labor and overhead unit costs. Because fatty acids contain no glycerine, the yield of anhydrous soap is 4 to 8% higher than from the corresponding neutral fat which, on a comparable per pound cost basis, shows a substantial raw material saving in favor of fatty acids. If pure uniform fatty acids are used, a fatty acid of different type may be blended, from which a soap may be produced with all desirable properties without boiling and graining out.

(5) Synthetic Fatty Acids

The production of fatty acids by oxidation of paraffin was developed mainly in Germany. The production of synthetic fatty acids reached 40,000 tons in 1939 and about 80,000 by the end of World War II. In a compre-

[42] U. S. Pat. 2,457,611.

[43] Personal communication, W. C. Ault, Eastern Regional Research Laboratories, U. S. Dept. Agr., Philadelphia, Pa.

[44] D. Stingley, *Soap, 21*, No. 2, 63–64 (1945).

hensive report on synthetic fatty acids, Wittka[45] points out that the chief raw materials of synthetic fatty acids are the synthetic paraffins produced from the Fischer-Tropsch process. Although the process normally yields only about 10% paraffin when it is carried out under a pressure of fifteen atmospheres, this yield can be increased to 50%. Under such a condition, the synthesis can be used to produce paraffin economically for the manufacture of fatty acids. The nonparaffin by-products of the Fischer-Tropsch process are hydrocarbons of low molecular weight, including naphthas, light mineral oils, etc. The crude paraffin wax obtained by synthesis is a mixture of the straight-chain hydrocarbon homologs with a wide range of molecular weights. For the oxidation to fatty acids, the hydrocarbons must be separated by fractional distillation, as the higher and lower fractions cannot be utilized in soapmaking. The most desirable fraction for oxidation contains the paraffins from $C_{18}H_{38}$ to $C_{28}H_{58}$, with an average molecular weight of 284. These hydrocarbons, when oxidized, yield fatty acids with an average molecular weight of 214, corresponding to fatty acids of the formula $C_{13}H_{26}O_2$, with properties corresponding to a mixture of lauric acid, $C_{12}H_{24}O_2$, with myristic acid, $C_{14}H_{28}O_2$. This fraction of hydrocarbons has an initial boiling point of over 350°C. Some of the paraffins formed by the Fischer-Tropsch method have molecular weights as high as 8,500, corresponding to the formula $C_{600}H_{1202}$. These can be used for other purposes, but they are of no use in the synthesis of fatty acids, for the acids so formed make soap totally lacking in detergent power. The fraction used for oxidation is a semi-solid white mixture of paraffin hydrocarbons. This soft white fraction is commonly called Fischer-Gatsch. The chemical reactions of the oxidation are not yet definitely known, but it seems evident that the first reaction consists in the interpolation of one oxygen molecule between the carbon and hydrogen atoms of one of the CH_2 groups of the paraffin molecule.

$$R-CH_2-CH_2-CH_2-R + O_2 \rightarrow R-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{\overset{|}{\underset{|}{C}}}}-CH_2-R$$
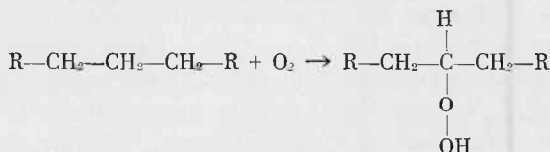
This equation seems to be correct, as it was found that the C—C is stronger than the C—H bond. The peroxides formed as the first product of oxidation are unstable and break down to form aldehydes and alcohols, which are in turn oxidized further and converted into fatty acids:

$$R-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OOH}{|}}{C}}-CH_2-R \rightarrow RCH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-O-CH_2-R \rightarrow R-CH_2-CHO +$$

$$R-CH_2-OH \rightarrow 2R-CH_2CHO + O_2 \rightarrow 2R-CH_2-COOH$$
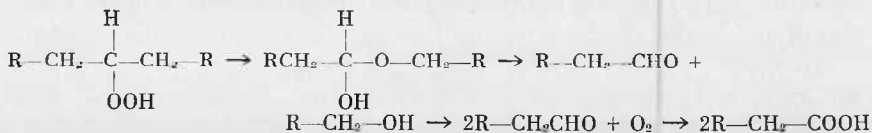
[45] F. Wittka, *Soap*, 16 (1940): No. 8, 28–32, 73; No. 9, 34–37, 73.

Of course, other reactions are possible and can be used to explain the many oxidation products. Since the paraffin molecule contains so many CH_2 groups, all practically identical in chemical properties, it is to be expected that the oxidation will not begin at any particular CH_2 group, but on any or every group without regard to position. That this is the case is verified by the fact that the fatty acids produced by this method have a large range of molecular weights. The oxidation of the Fischer-Gatsch paraffins results in the formation of all the homologous fatty acids from formic acid to octadecanoic acid.

The manufacture of synthetic fatty acids follows these general steps: (1) Pretreatment of the paraffins. (2) Oxidation in the presence of catalysts. (3) Separation of the oxidation products. (4) Purification of the fatty acids.

Pretreatment means the fractional distillation of the paraffin in such a manner that only paraffins of the following composition remain.

Paraffins with 19 to 22 C atoms 27.4%
              22 to 25 C atoms 31.0%
              25 to 27 C atoms 23.7%
              27 to 28 C atoms 11.7%
          Over 28 C atoms 1.7%

The average molecular weight of this hydrocarbon mixture is 284, corresponding approximately to the formula $C_{20}H_{42}$. Besides, pretreatment means the subjecting of these paraffins to the actions of strong oxidants. Adding previously oxidized paraffins also has the effect of speeding up oxidation. The actual oxidation[46] may be carried out at and above 160°C. in aluminum vessels with an alloy steel head (Fig. XV-5). At Witten, there are 12 vessels, each of 20 tons capacity, and 24 vessels of 10 tons capacity. Eight of the latter are made entirely of alloy steel (chrome nickel), but these are not as satisfactory as the aluminum vessels, since this metal catalyzes the oxidation reaction. Alloy steel heads are necessary, however, since aluminum is corroded by the low molecular volatile fatty acids. The 20-ton vessels are 9 meters high and of 2.7 meters interior diameter. Each vessel is provided with an air distributor, a bottom dished coil for heating and a middle coil for cooling, the oxidation reaction being exothermic. The air distributor and pipes are made of chrome nickel steel. The air distributor has a diameter of 1.2 meters, the top being provided with 1 mm. holes and the bottom with 3 or 4 large holes. Such a vessel is shown diagrammatically in Figure XV-5. The oxidation is carried on only until about 30% of the Gatsch has been oxidized. Experience has shown that further oxidation results in the formation of undesirable products such as ketones. The low molecular weight or

[46] "Production of Synthetic Fatty Acids and Edible Fats, Deutsche Fettsäurewerke, Witten," by E. L. Baldeschwieler. Report No. 225, Office of the Publication Board, U. S. Dept. Commerce, Washington, D. C., 1945.

volatile acids are condensed, absorbed in water, and separated into two layers. The lower layer consists of an aqueous solution of formic, acetic, and some propionic acids, the upper layer being a mixture of C_3–C_{10} acids. The
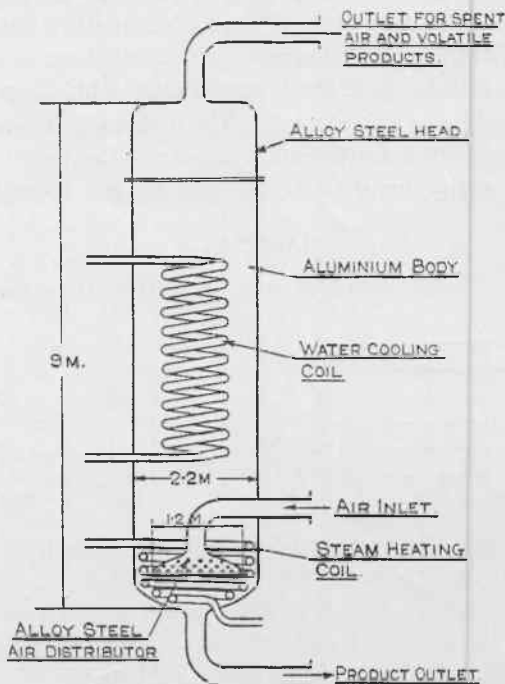
Fig. XV-5. 20 ton kettle for wax oxidation.[46]

formic acid is used for the treatment of fodder silos and the acetic acid for esterification of cellulose. The water-insoluble acids are sold for the manufacture of plasticizers, perfumes, etc. The wash towers are 11 meters high and are provided with Jena glass lines to prevent corrosion by the water-soluble acids. In the oxidation vessels, 8–20 tons Fischer-Tropsch Gatsch is charged together with 0.2% potassium permanganate in 15% aqueous solution. At 110°C. 50 cubic meters of air per ton of paraffin Gatsch is blown through for a period of 20–24 hrs. About 50–70% of the Gatsch remains as unsaponifiable and is separated from the oxidation product by saponifying the latter with the calculated amount of 38° Bé NaOH solution. The reaction products separate into two layers. The upper layer consists of unreacted Gatsch and is returned to the oxidation vessel. The lower layer is an emulsion containing 30% soap and 30% Gatsch which is fed into an autoclave and heated for one hour at 170–180°C. and 25 atm. pressure. This treatment causes a further separation of Gatsch, which is returned to the oxidation

vessel and a lower layer of soap solution containing 45% soap and 15% Gatsch. The soap solution is then fed to a pipe still heated by gas at 320°C. for soap acids and 380°C. for edible acids when the water and remaining Gatsch are driven off. The Gatsch is recycled. The anhydrous soap is then run directly into water to form a 40% solution and the fatty acids liberated by addition of sulfuric acid. This reaction is carried out at 90–95°C.

The vacuum distillation of the liberated fatty acids is carried out in four stages, corresponding to the four cuts. The first stage (*Vorlauf* or light fraction) is provided with a fractionating column. The next two stages are in parallel (*Hauptlauf* or main fraction), and the last stage is for the heavy

TABLE XV-5

	Light fraction (*Vorlauf*)	Main fraction (*Hauptlauf*)	Heavy fraction (*Nachlauf*)	Residue (*Rückstand*)
Temperature, °C.	up to 120	120–170	270–315	—
Yield, %	15–20	55–60	7–12	7–13
Mol. wt.	C8–C10	C10–C20	C21–C28	—
Neutralization No.	450–460	245	155–160	80–90
Saponification No.	450–460	255	175–180	110–120
Esterification No.	0–1	10	20	30
Unsaponifiable matter, %	0	1.5	10.0	—

fraction (*Nachlauf*), the residue being collected from the kettle of the last stage. The distillation is carried out in the presence of 5% of steam; the total steam consumption, including the vacuum steam injectors, is approximately equal to the weight of acids treated. Composition of the fractions is shown in Table XV-5. Total yield of fatty acids is 80% of the still charge.

The fatty acids from the main fraction are the main raw material of interest to the soap industry. (In Germany, some of those synthetic acids were esterified with glycerine for the production of edible fat.) The fatty acid fraction that can be used in soapmaking is a soft yellowish product with the following properties:[47]

Solidification point	26.2°C– (30°C.)
Odor	practically none
Acid value	244.2 (239)
Saponification value	247.2 (239.5)
Average mol. wt.	229.8 = $C_{15}H_{27}COOH$
Iodine value	4.9
Hydroxyl value	3.7
Naphtha insoluble	0.0%
Unsaponifiable matter	0.29%

A note by the Fuel Research Station DSIR in Great Britain[48] mentions the fact that the German synthetic soap possessed excellent lathering power, but had the property of leaving an unpleasant odor on the skin after use, and

[47] F. Wittka, *Soap*, 16, No. 9, 73 (1940).
[48] *Food*, 15, 128 (1946).

the synthetic acids were used in toilet soaps only to the extent of 20 to 30% of the total fatty acid content. Further, it is pointed out that, at present, the process is rather uneconomical. Under the best conditions achieved in Germany, the production of a ton synthetic fat or soap requires 60–70 tons of coal.

How far this process is feasible from an economic point of view under normal conditions is difficult to assess, but it may be surmised that improvements are possible, and that the process may also find applications under normal peacetime conditions. Synthetic fatty acids are also produced in Russia, but we do not know how successfully. The effect of different catalysts on the oxidation of paraffin was described by H. Pardun and R. Kuchinca.[48a]

Quite another approach to the problem of the synthesis of fatty acids is described in the British patents 605,848–49 (1948) held by E. I. du Pont de Nemours & Co. The synthesis consists in the condensation of ethylene with a short chain saturated fatty acid such as acetic, propionic, isobutyric, etc. acid to give a saturated fatty acid with a chain length of practically any desired length. A small percentage of catalyst, some tenth per cent of the reaction mixture, is used. Catalysts mentioned are hydrazine sulfate, dibenzylhydrazine, or even a few parts per million of oxygen. Higher amounts of oxygen (over 100 p.p.m.) interfere with the reaction. Thus the ethylene used must be freed from larger amounts of oxygen, acetylenic, and other similar type impurities by a special pretreatment. The reaction may be written as follows:

$$n(CH_2{=}CH_2) + H{-}R_1R_2CCOOH \rightarrow H(C_2H_4)_nR_1R_2CCOOH$$
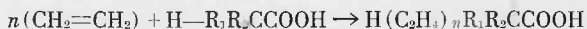
where R_1 and R_2 may be hydrogen, monovalent H groups, etc. In one example 100 parts isobutyric acid was condensed with 112 parts ethylene at 250°C. and 850–950 atmospheres of pressure. This results in a 11.5% yield (acid basis) of a fatty acid having a molecular weight of 728, i.e., a calculated chain length of C_{50}. In another example, using a lower ratio of ethylene, a yield of 16.5% (acid basis) of a fatty acid with a molecular weight of 346 (C_{22}) was obtained. How far this method will be of immediate interest for the soap industry remains to be seen. The very high pressure somewhat warrants against immediate large scale production as equipment would be extremely expensive, especially if large batches are to be produced. However, the approach to the synthesis of fatty acids is quite an interesting and original one, so this short description should be of interest here.[48b]

[48a] H. Pardun and R. Kuchinca, *Erdoel u. Kohle*, *3*, 109–120 (1950). See also H. Anders, *Fette u. Seifen*, *54*, 77–80 (1952).

[48b] J. W. McCutcheon, *Soap & Sanit. Chem.*, *28*, No. 1, 83 (1952).

(6) Naphthenic Acids[49]

These acids are by-products of the petroleum industry and have found use as a fat raw material for the soap industry only to a relatively small extent. In Russia, where the crudes are usually rich in naphthenic acids, they are used to a somewhat greater extent. The naphthenic acids cover a class of cyclic acids in a range of molecular weights from the lowest possible to the order of 1000 or more. At present, the identity of the naphthenic acids as carboxyl derivatives of naphthenes is regarded as having been established, although the exact structures involved are still being worked out. At the same time, the presence, in smaller portions, of the conventional fatty acids is being recognized. The recovery of naphthenic acid is achieved by the alkali wash of different petroleum fractions and subsequent refining of the crude naphthenic soaps obtained. The acids vary considerably in their chemical composition and analytical data. Some typical commercial products in the United States show the following data:[49]

	Type A	Type B
Neutralization number	299	167
Combining weight	188	335
Purity, % naphthenic acids	—	85
Sulfur, %	0.69	0.58
Specific gravity	0.978	0.980
Pour point, °F.	—	+5
Distillation: 10%, °F.	472	
80%, °F.	567	
% at 500°F.	36	
Color	Light yellow	Trace

It is somewhat undeserved that naphthenic acids are not used to a greater extent in the soap industry. The sodium soaps of most naphthenic acids have somewhat similar properties as the soaps of coconut oil; they are easily soluble and quick lathering; they are not easily salted-out, as they are very resistant to electrolytes. The latter fact makes them valuable raw material for the production of sea water soaps. J. Davidsohn proved that most naphthenic acid soaps are salted-out only with even higher concentration of NaCl solution than coconut or palm kernel oil soap. He produced, on a laboratory scale, a hard soap from a fat stock of 33% coconut oil, 33% tallow, and 33% refined naphthenic acid.

It is possible that naphthenic acids are not used to a great extent in the production of common soaps because they are valuable raw materials for different metal soaps, which are used as siccatives in the paint and varnish industry and for rotproofing of textiles (copper naphthenates) and ship bot-

[49] W. A. Gruse and D. R. Stevens, *The Chemical Technology of Petroleum.* 2nd ed. McGraw-Hill, New York, 1942, p. 97.

tom paints.   Besides, many special synthetic detergents and emulsifying agents are produced on the basis of sulfonated naphthenic acids.

Naphthenic acid soaps with triethanolamine are clear liquid products which are useful additions to liquid soaps for clarifying and lowering the temperature at which they congeal or develop turpidity.[50]   Only highly refined, practically odorless grades of naphthenic acids are suitable for this special purpose.

[50] W. H. Dickens, *Soap, Perfumery & Cosmetics, 10,* 490 (1937).
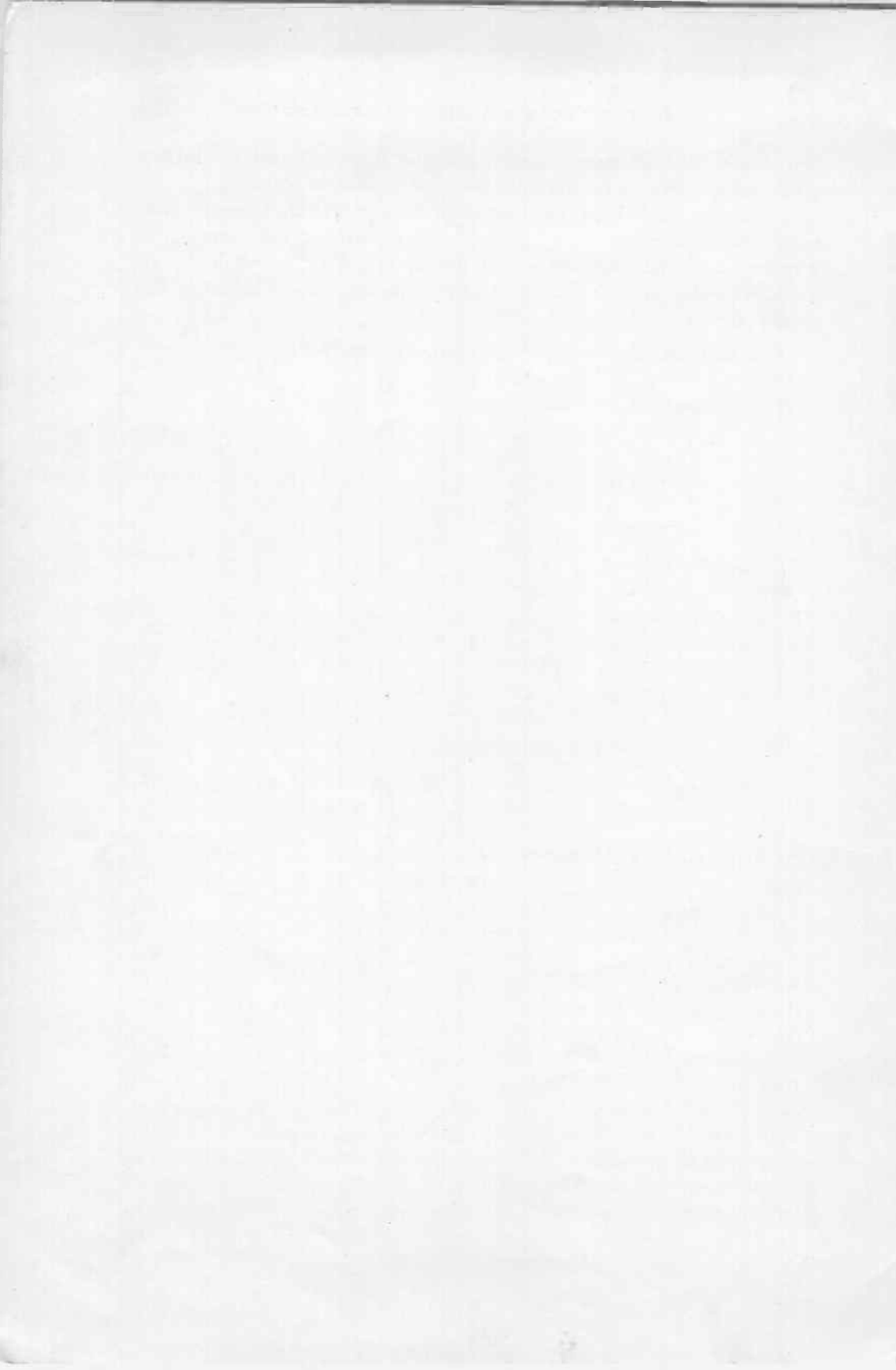
INDIVIDUAL FATS AND OILS

The individual fats and oils that are especially important raw materials for the soap industry will be discussed in this chapter. The specific property that each fat and oil gives to soap and its special use for the soapmaker will be pointed out in detail. (See also Table XII-7.) The analytical data and composition of the different oils and fats are given in Table XII-4.

(I) VEGETABLE OILS AND FATS

(1) Linseed Oil and Some Other Drying Oils of Similar Properties

(A) LINSEED OIL

This oil is obtained from the seed of the flax plant, *Linum usitatissimum*, which is extensively grown in the Argentine, Canada, India, Russia, and the United States. The flaxseed produced in the United States is grown largely in North and South Dakota, Minnesota, and Montana. The oil is usually extracted by hot pressing with either hydraulic or automatic expeller presses. Usually, the seed contains about 40% oil. 6% oil generally remains in the oil cake. Linseed oil is a drying oil (for characteristics see Table XII-4). The crude oil contains mucilaginous, carbohydrate, and protein substances which settle on standing in storage tanks. For soap manufacture, these settled crude oils are a valuable raw material mainly for the production of potash soaps. Further refining of linseed oil is carried out, if necessary, according to the usual refining process. Alkali refining removes the gum, coloring matter, etc. and definitely improves the oil for soapmaking. If further bleached with carbons and bleaching earth (2–3%), a very superior white oil is obtained, excellent for potash soap production. But linseed oil

may be used even for the production of yellow household soap. Linseed oil is easily saponified with caustic lyes of 12–15° Bé. It is standard practice to start saponification with lyes of 12–15° Bé and to complete the saponification with lyes of 20–25° Bé strength. Linseed sodium soap may be salted-out with caustic soda solution of about 9° Bé or brine solution of 6° Bé. If produced "on niger," linseed oil hard soap contains 50–60% fatty acids. This soap is rather soft and has a yellow or yellow brown color. It is easily soluble in water and gives a copious foam. It is not suitable to use linseed oil alone for the production of hard soap. The soaps have very poor keeping quality and, after a comparatively short time, give off a disagreeable odor and dark stains appear on the surface of the soap cake. Even in combination with saturated fats and oils, which form hard soaps, discoloration may appear in the finished soap cake. But, according to Kranich,[51] the use of linseed oil in amounts varying from 15 to 25% blended with the other oils or their acid derivatives should not change the finished product to any great extent. The use of linseed oil should assist in the production of soaps made solely from fatty acids by having present in the batch a sufficient percentage of neutral oil for subsequent smooth boiling for those factories not having proper mechanical equipment for the manufacture of soaps when using fatty acids alone. Stability and odor when using these limited proportions of linseed oil are not too serious a drawback. It is possible to use inhibitors which prevent oxidation of the soap or to use linseed oil in combination with rosin, whereby it may be possible to eliminate the danger of spot formation or the occurrence of fishy odor. Soaps from double distilled linseed *fatty acids* are less prone to discoloration and odor deterioration and show good properties even if used in high percentage of the fat stock.

But the main use of linseed oil in soap manufacture is for the production of soft potash soap. If only caustic potash lye is used for saponification, a yield of 235–240% may be obtained. The pure potash soap is greenish yellow to reddish yellow. More information about soft soaps from linseed oil will be given in Chapter XIX, 3.

(B) PERILLA OIL

An oil with properties similar to linseed oil, *perilla oil,*[52] is obtained from the seeds of the *Perilla frutescens* and related plants of the *Labiatae* family cultivated mainly in Northern India, Japan, Korea, and Manchuria, as well as in Brazil. The average oil content of the commercial seed is about 38%, but may vary in oil content between wide ranges (30–51%). The oil is not very

[51] H. Kranich, *Soap*, 20, No. 3, 27–28 (1944). E. J. Better, *Allgem. Oel u. Fettztg.*, 29, 6 (1932).

[52] G. S. Jamieson, *Vegetable Fats and Oils*, 2nd. ed., Reinhold, New York, 1943, pp. 288–289.

suitable for the production of hard soap but in smaller percentages it may be used in potash soaps (see Table XII-4 for characteristics).

(C) Poppy Seed Oil

This oil[53] is obtained from the seed of various varieties of the plant *Papaver somniferum,* which has been cultivated for centuries in Europe, China, India, Asia Minor, Egypt, and elsewhere. The seeds, which are white, brown, bluish gray or bluish black, contain from about 44 to over 50% of oil. The white seed is considered to yield the finest oil. It is customary to make a cold pressing, then a hot pressing. This highly unsaturated oil is used mainly for edible purposes, but the darker grades find their way into the soap pan. The oil is not suitable for the production of any but soft soap, for which it is a high-grade raw material, giving a transparent reddish soft soap of excellent foaming quality and high detergency (for characteristics, see Table XII-4).

(D) Hemp Seed Oil

Hemp seed oil is produced from the seed of the plant *Cannabis sahoa,* mainly cultivated in India, Manchuria, Europe, France, Italy, and Russia. Experiments with hemp seed have been made even in the United States. The seeds, containing 32–35% oil, according to Jamieson, are either solvent-extracted or pressed. The oil has a greenish color and is used in the soap industry for the production of green soft soap (see Table XII-4).

(E) Niger Seed Oil

Niger seed oil is obtained from the plant *Guizota abyssinica,* which grows in some parts of tropical Africa and India. The weight of the seeds containing 38–50% oil is only about 0.035 gram. Usually, the seed is pressed twice, cold and hot. The light-colored oil is used for edible purposes, but is sometimes used for soap manufacture. The oil is much less drying than the oil previously described. Soaps are practically never produced from niger seed oil alone. But in the pan charge it may be used to replace soybean or sunflower seed oil.

(2) Soybean Oil

Soybean oil is obtained in large quantities from the seed of the many cultivated varieties of the legume *Glycine max L. Merill,* cultivated since early times in China and other parts of the Far East, but also cultivated in more recent times practically in every part of the world. The largest producing countries are China, Manchuria, and the United States. The beans are largely grown in the corn belt of the United States. About one-half of the

[53] G. S. Jamieson, *loc. cit.*, p. 292.

oil in the United States is obtained by the expression method, the other half being obtained by solvent extraction.

Soybeans have an average oil content of 17–22% and, in addition, contain lecithin (see Ch. XII-1). An average yield from 1 ton of soybeans is about 350 lbs. of oil and 1600 lbs. of cake. For soap manufacture, both crude oil and refined oils are used. It is easily saponified with 10–12° Bé NaOH. Pure salted-out soybean oil sodium soap is hard and light yellow or green, but is not easily soluble and does not give a sufficient foam. Thus, it must be blended especially with coconut oil to give the necessary foam and detergent power. In this case, 20–30% in the fat stock may be used. Soybean oil soap is salted out with 8.5 Bé NaOH or 6 Bé NaCl. For the production of soft potash soap it is a very suitable raw material, as the potassium soap foams much better than the sodium soap. The soft potash soap has a reddish yellow color, it is transparent, and it is heat resistant. For the characteristics of soybean oil—a drying oil—see Table XII-4.

(3) Sunflower Seed Oil

This oil is obtained from several varieties of *Helianthus annuus*. Sunflowers are cultivated mainly in Russia, the countries of Southeast Europe, China, India, and Argentina. The seed contains 22 to 23% oil; the kernels, which form 49–54% of the seed, contain about 50% oil.[54] The seed is either freed from the hull or is pressed or extracted as whole seed. The cold-pressed oil is a high-grade edible oil, but the lower grades, usually unrefined, are used in the soap industry. It is a yellow oil of the semidrying type which very often appears turbid. The turbidity derives from the waxy coating of the seed and some mucilaginous substance left in the raw oil. Sunflower oil may be used in rather high percentages for the production of hard soap. In Russia, the oil is even used as 100% fat stock for the production of hard soap.

Taking into consideration, however, that the oil contains only about 8% solid fatty acids, it would appear to be unsuitable as a raw material for hard soap. Soap from sunflower oil has poor keeping quality and is rather soft. But the use of sunflower seed oil in combination with other harder fats has many advantages, since it imparts a very homogeneous structure to the soap. The oil is not easily saponified. Very weak lyes are used to start saponification. Stronger lyes are used to complete the saponification process. Soap from sunflower seed oil is very sensitive to electrolytes. It is completely salted-out by caustic soda of 7° Bé or brine solution of 5° Bé. It is of advantage to saponify first the sunflower seed oil completely and then to add the other components of the fat stock and saponify them in the sunflower oil soap

54 E. J. Better, *Allgem. Oel u. Fettztg.*, 29, 211 (1932).

in the pan. Potash soaps may be produced from sunflower seed oil alone, giving a yield of 235–240%. These soaps have a pleasant breadlike odor, but it is common to cover this odor by the use of rosin.

Mention must be made of the fact that in Russia especially sunflower oil is hydrogenated to give fat of different degrees of hardness. This hydrogenated sunflower seed oil (*Salomass*) is then used for the production of hard soaps—even toilet soaps. For characteristics see Table XII-4.

(4) Cottonseed and Kapok Oil

Cottonseed oil has great importance not only as an edible oil, but also as a soap oil. Cottonseed oil is obtained from the seeds of various species of the plant *Gossypium*. The oil is a by-product of the processing of the plant for fiber. The world's greatest cotton producing region is Southern United States; other important producing countries are India, China, Russia, Egypt, and Brazil. The average yields of the various products resulting from the processing of one short ton of cleaned seeds are approximately as follows:

Linters	143 lbs. or	7.15%
Hulls	520 lbs. or	26.0%
Oil cake	906 lbs. or	55.3%
Crude oil	312 lbs. or	15.6%
Loss (principally moisture)	120 lbs. or	6.0%

Crude cottonseed oil has a strong, characteristic flavor and odor and a dark, reddish brown color from the presence of pigments and other highly colored material extracted from the seed. Its free fatty acid content and general quality depend to a considerable extent upon the weather prevailing during the time that the cotton stands in the field after coming to maturity. Hence, the quality of crude oil will vary in any given locality from year to year, being highest in dry seasons and lowest when the seed is exposed to wet weather in the fields, or stored with a high moisture content. The free fatty acid content of the best North American oil will vary from 0.5 to 1.0%, although oil containing 1.5 to 3.0% of free acids is not uncommon, and the free acid content of oil from wet or damaged seeds may be as high as 5% or more. In the United States, where elaborate trading rules have been evolved for dealing in cottonseed oil, the grade and price of the oil are not established from the characteristics of the crude oil, but are based upon the yield of oil obtained by a standard refining test, and the color of the refined oil. The crude oil refines by caustic soda treatment to a relatively light color, *i.e.*, good oil may readily be refined to a color on the Lovibond scale of 35 yellow and 4 to 7 red. As the free fatty acid content of the oil increases, there is a corresponding increase in the refining loss, coupled with a more or less progressive increase in the color of the refined oil.[55] It must be pointed out

[55] A. E. Bailey, *Industrial Oil and Fat Products*, 2nd. ed., Interscience. New York, 1951, p. 151.

that, for the soap industry, practically all cottonseed oil is refined oil, as the color of the crude oil would darken the soap to a considerable extent. The very dark soapstock from the refining of cottonseed oil is usually split with sulfuric acid and the fatty acids distilled (see Ch. XV-2). The distilled fatty acids are of light color and a valuable raw material for the soap industry. The soapstock is sometimes used as such for the production of low-grade hard or soft soap, but fatty acid distillation methods are preferred.

The refined cottonseed oil, as it is used for the production of soap, has a yellow brown color (for characteristics, see Table XII-4). The oil is saponified with 10–12° Bé caustic lye, but it is of advantage to saponify a mixed fat stock. The sodium soap from cottonseed oil alone has a yellow color, it may be salted out with 8° Bé NaOH or 5.5° Bé NaCl to a low fat stock soap of around 59%. The most common practice is to use cottonseed oil in the fat charge in combination with tallow, grease, and coconut oil. Potash soap from cottonseed oil is yellow and turns turbid after some time. Soap with too high a percentage of cottonseed oil in the pan charge has poor keeping qualities, and spots, and discolors frequently. Cottonseed oil should never be used in high-grade toilet soap.

An important by-product of the production of edible cottonseed oil is *cotton stearine*. This is a fat of a high melting point, about 30–40°C., but very often lower, obtained by the winterizing process in which the refined oil is chilled and maintained at low temperature, about 0°C. The high melting constituents of the oil are crystallized and filtered off. The quantity of stearine separated in wintering cottonseed oil depends somewhat upon the source of the seed from which the oil was obtained. Oil from India generally yields less stearine than oils from America and Egypt. In the United States, the stearine separated usually varies from 12 to 25% of the oil, 16 to 18% being common.[56] Often the yield of stearine from a given oil varies considerably at different plants because of variation in the conditions in the chillroom. Cottonseed oil stearine gives corresponding harder soaps. The following characteristics for cotton stearine are given by Grün and Walden.[57]

Specific gravity (15°C.)	0.9188
Melting point, °C.	20–40
Solidifying point, °C.	16–32
Saponification value	194.6–195.1 (198.4)
Iodine value	88.0–103.8

The titer of the fatty acids of cotton stearine usually lies between 21–23°C.

This is a typical analysis, which shows that cotton stearine still contains a large percentage of unsaturated fatty acids. In a sense, cottonseed oil

[56] G. S. Jamieson, *loc. cit.*, p. 213.

[57] A. Grün and W. Walden, *Analyse der Fette und Wachse*, Vol. 2, Springer, Berlin, 1929, p. 129.

TABLE XVI-1[58]

Change in Composition of Cottonseed Oil through Progressive Hydrogenation

Iodine value	% linoleic	% oleic	% isooleic	% satd. acid
104.0	48.4	23.4	0.8	26.7
87.5	29.2	42.9	6.1	27.4
73.6	13.9	57.6	11.3	27.3
64.1	3.6	67.4	16.8	28.8
59.7	0.7	68.0	21.0	30.0
55.2	—	—	22.7	33.9
49.9	—	—	21.1	38.5
42.7	—	—	19.0	47.5
34.7	—	—	15.8	57.0

stearine gives to a soap the same properties as peanut oil. Hydrogenated cottonseed oil is a very valuable raw material for the soap industry. Its characteristics and the characteristics of a soap produced from the fat depend on the degree of saturation obtained by the hydrogenation process.

The effect of hydrogenation with a good selective catalyst is shown in Fig. XVI-1.[59]

An oil with properties similar to cottonseed oil is *kapok oil*, which is rarely available as a raw material for soap manufacture. The oil is obtained
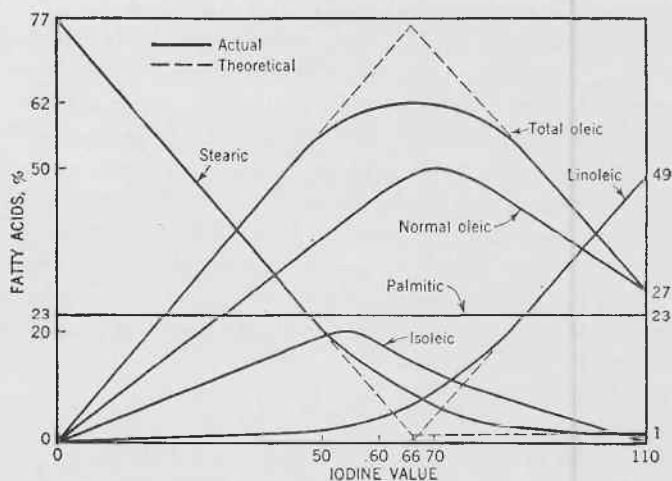
Fig. XVI-1. Composition of selectively hydrogenated cottonseed oil.[59]

[58] G. S. Fisher, R. T. O'Connor, and F. G. Dollear, *J. Am. Oil Chem. Soc.*, 24, 382–387 (1947).

[59] A. E. Bailey, ed., *Cottonseed and Cottonseed Products*, Interscience, New York, 1948, p. 712 (Fig. 184).

from the tropical tree *Ceiba pentandra.* The whole seed contains about 20–25% oil, the kernels about 40%.

(5) Corn Oil

Corn oil, or maize oil, a semidrying oil, is obtained from the germ of the maize, *Zea mays.* It is produced principally in the United States and to a lesser extent in South Africa, Argentina, and Canada. Although the germ contains approximately 50% oil, the oil content on the whole seed is not more than 3–6.5%. This semidrying oil is more or less a by-product of starch and glucose manufacture.[60]

The production of corn oil is carried out somewhat differently from the usual methods for oil-bearing seeds. The corn, after cleaning, is placed in large tanks, where it is soaked with water containing sulfur dioxide (SO_2). During this process, the hull is loosened from the kernel. The kernels are then run through *attrition mills,* which break away the germ from the kernel. The germ is then separated in a water tank, where the germ, owing to its oil content, floats on the surface and is skimmed off. Finally, before grinding and pressing (expelling), the germ is washed and dried. The crude oil, with a free fatty acid content of about 3%, is usually golden or dark yellow, and if freshly extracted has a distinct odor of corn meal (see Table XII-4). The refining process, if necessary, is along common lines.

Saponification is accomplished easily with NaOH of 12–16° Bé. The pure corn oil sodium soap is completely salted-out with NaOH of 7° Bé or NaCl of 5° Bé. The sodium soap, with regard to color, consistency and detergent property is very similar to soap from sunflower seed oil. The sodium soap is a yellow or light brown soap and rather soft. Thus, corn oil is seldom used alone for the production of soap bars, but, like sunflower seed oil, it may be used in combination with harder fat stock. For high-grade solid soap, it should not be used in amounts exceeding 10% of the fat charge. However, it is widely used for soft potash soap. The soap is similar in properties and color (a reddish tint) to that produced from soybean oil. Hydrogenated corn oil yields a valuable raw material even for higher grades of hard soaps.

(6) Sesame Seed Oil

This oil belongs to the class of semidrying oils. It is the oil of the plant *Sesamum indicum* and is produced chiefly in the Middle East, some parts of Africa, China, and India. The seeds, varying in color from white to yellow, brown, and black, contain 50–57% oil and are usually extracted by pressing. It is a high-grade edible oil, but some of the lower grades and the

[60] M. M. Durkee, *Food Inds.,* 3, 251 (1931).

soapstock fatty acids are finding their way into the soap pans. The crude sesame oil varies in color from amber to yellow and refines to a pale yellow.[61] "Sesame oil is relatively high in unsaponifiable substances, but these consist largely of sterols and other substances which are not removable by refining. It is relatively low in other nonoil materials. The unsaponifiable fraction of sesame oil contains a class of substances, sesamin, sesamolin, etc., which give distinctive color reactions . . . , hence, sesame oil is readily detected even in small amounts in other oils, even after hydrogenation. The unusual stability of sesame oil is possibly attributable to the antioxidant effect of some of the same substances." For characteristics of the oil, see Table XII-4.

For the soap industry, sesame oil may be used in combination with other fats and oils mainly for the production of household soaps. At a time when "mottled" soaps were produced on a larger scale than today, sesame oil was used in combination with olive oil for the production of "mottled" household soap of the Marseilles type. Sesame oil alone gives a grey to yellow soap which is not soft but plastic in texture. It is not difficult to saponify and the soap may be finished on niger. The soap is completely salted-out with a NaOH lye of 8° Bé or by a 5.5° Bé brine solution. For the production of soft potash soap, sesame oil is very suitable; it gives a light brown, transparent soap which is highly resistant to temperature changes.

(7) Rape Seed Oil (Colza Oil)

This oil, a semidrying oil, derives from the seeds of *Brassica rapa* and similar related species. The seeds are grown extensively in Europe and Asia and yield between 30 and 45% oil when extracted by pressure or by a solvent process. The crude oil is dark in color, yellow or amber, and refines to a yellow oil. The crude oil contains considerable quantities of phosphatides and other impurities. The refined oil has a characteristic pungent, mustard-like odor, which is removed by deodorization. However, deodorized rapeseed oil is somewhat inclined to revert in flavor and acquire an unpleasant taste different from that of the undeodorized oil. Refined or otherwise processed rapeseed oil is often called colza oil. It is not a high-grade edible oil, and for this reason is widely used—especially in Europe—in combination with other fats and oils for the production of common household soap (see Table XII-4).

It is very difficult to saponify the oil with dilute lyes, since the soaps are very sensitive to electrolyte. The soap is salted out with NaOH of 5.5° Bé or brine (NaCl) solution of 3.5° Bé. It is thus practically impossible to pu-

[61] A. E. Bailey, *Industrial Oil and Fat Products*, 2nd ed., Interscience, New York, 1951, p. 160. E. J. Better, *Seifensieder Ztg.*, 58, 574 (1931) ; *Les Matières Grasses*, 9331 (1931).

rify the soap by finishing on "niger." On the other hand, rape oil produced on spent lye is brittle and crumbles between the fingers. For this reason, it is possible to use rape oil only in combination with other fats and oils. The soft potash soaps produced purely from rape oil are not resistant to temperature changes. Thus, for soft soaps as well, rape oil may be used only with other oils.

(8) Peanut (Arachis, Ground Nut) Oil

This very valuable oil for the soapmaker is also a high-grade edible oil. The lower grades or the fatty acids from the soapstock are usually used in the soap industry. The oil—a nondrying oil—is derived from the seeds of the legume *Arachis hypogaea* with its different varieties.

Peanuts are grown in practically all parts of Asia, some parts of Africa, in the United States, and in Spain. Shelled peanuts contain about 45–50% oil, which is usually extracted by means of expellers or hydraulic presses. Solvent extraction is rarely used. Commercial grades of crude oils vary according to the care taken in extracting the oil and the quality of the peanuts themselves, from light yellow to a reddish or even dark brown color. The oil is filtered and allowed to stand in tanks until the foots have settled. Peanut oils will rapidly become rancid, as will other oils, when brought into contact with other rancid oil or fermented foots. The crude oil is refined by the usual methods. The fatty acids of the soapstock are used for soap production, but for high-grade toilet soaps even refined, but usually not deodorized, oil is used. Crude peanut oil finds its way into the soap pan as well (see Table XII-4).

Saponification of peanut oil is easy, especially if a certain amount of free fatty acids (2–6%) is present. The concentration of the caustic lye used may be as high as 15–18° Bé. The soap is completely salted-out with NaOH of 7.5° Bé or NaCl of 5.5° Bé. Soap from peanut oil is relatively hard if grained-out on spent lye, but rather soft when produced on niger. Thus, peanut oil is usually saponified in combination with other fats and oils; a combination of 50% peanut oil with 25% tallow and 25% coconut (or palm kernel) oil gives a very good household chip soap of excellent solubility characteristics. For toilet soap, lower percentages of peanut oil and combinations with tallow and coconut or palm kernel oil are advisable. In the production of soft potash soaps, peanut oil is especially suited for the so-called "figged" soft soaps or "silver" soaps (see Chapter XIX). The reason for this is the high percentage of high melting fatty acids present in the oil. The potassium soaps from these higher melting fatty acids crystallize on standing.

Mention must be made of the fact that hardened peanut oil is an important raw material not only for the edible fat industry but for the soap industry as well.

(9) Almond Oil

This is an oil with similar properties to peanut oil. Almond oil is usually too high priced to be used for the production of common soap. But for the production of very high-grade toilet soaps or medicated soaps, almond oil finds its use in the soap industry. It is easily saponified even by the "cold method." For characteristics of almond oil see Table XII-4. The sodium soap has excellent forming qualities and is very mild in its effect on the skin (see Chapter XXXII).

(10) Olive Oil

A nondrying oil, olive oil is obtained from the fruit of the tree *Olea europea,* of which about 300 varieties are known. The oil content of the fruit varies from 15 to 40%. The American olives usually contain about 30% oil. The higher grades of olive oils are mainly used for edible purposes. The fresh extracted oils are even used unrefined. Crude oils of lower quality with high percentage of free fatty acids, the "foots," and the "sulfur oils" are used in the soap industry. The soapstock fatty acids of refined olive oils are also raw materials for the soap industry. (For characteristics of pure olive oil, see Table XII-4.) For high-grade toilet soaps or special medical soaps, even the refined olive oils are used, but the *huile vierge* (virgin oil), the unrefined cold-pressed olive oil, is practically never used in the industry. Some characteristics of olive oil foots which are often used for soap manufacture are given in Table XVI-2, Standards of the American Oil Chemists' Society (A.O.C.S.), in comparison with edible olive oil.

TABLE XVI-2

Characteristic	Edible oil	Olive oil foots[b]
Specific gravity at 25/25°C.	0.909–0.915	—
Iodine value[a]	80–88	77–90
Saponification value	188–196	186–196
Titer, °C.	17–26	16–26
Unsaponifiable matter, %	Not over 1.4	Not over 2.3
Free fatty acids, %	Not over 1.5	—

[a] Minimum I.V. for California oils shall be 79. Maximum I.V. for African and Dalmatian oils shall be 92.

[b] Olive oil foots shall contain not over 3% moisture and insoluble impurities, and not over 0.20% ash.

Sulphur oils are dark in color and contain a high percentage of free fatty acids, up to 55%, some water, up to 2%, and 3–6% hydroxy fatty acids.[62] These hydroxy fatty acids give soaps which cannot be salted-out and which drag out soaps of nonhydroxy fatty acids into the spent lye as well. Thus,

[62] E. Manzella, *Z. Oel- u. Fettind., 40,* 393 (1920).

not only are the hydroxy fatty acids a total loss in the production of a hard soap, but in addition there is a loss of a percentage of soaps of nonhydroxy fatty acids which are also lost in the spent lye. This occurs whenever oil and fats with a high percentage of hydroxy fatty acids are used for the production of hard soaps. In addition, these acids complicate the lye treatment procedure for the recovery of glycerine and decrease yields there as well.

Olive oil itself is easily saponifiable if it contains some free fatty acids; otherwise, it is rather difficult. The sodium soap is hard, and, depending on the color of the oil used, is white, yellow, green or dark green. The soap may be finished on niger, but may also be salted-out on spent lye (with NaOH of *ca.* 7.5° Bé, or NaCl of 5.5° Bé). In the first case a somewhat soft soap, and in the latter case a very hard and brittle soap, are obtained. Pure olive oil soaps are very mild on the skin and are on the market as special olive oil castile soaps, baby soaps, and medicated soaps. Pure olive oil soaps are also used as textile soaps, especially for silk and other sensitive fibers. Olive oil in combination with other oils and fats is used for practically all kinds of hard sodium soaps. Soft potash soaps from olive oil are used mainly for medical purposes (see Chapter XIX).

(11) Olive Kernel Oil

This oil is either expressed or solvent-extracted from the kernels, which usually contain *ca.* 25–28% of oil. The oil is of yellow color and has a sweet taste resembling almond oil. Olive kernel oil may be used for soap manufacture either crude or refined. It is seldom used in percentages higher than 20% of the fat stock. The soaps of olive kernel oil have properties somewhat similar to those of the soaps from the olive oil itself (see Table XII-4).

(12) Castor Oil

Castor oil is otbained from the seeds of the plant *Ricinus communis* from either cultivated or wild plants growing mainly in tropical or subtropical countries (India, China, Manchuria, Mexico, and Brazil), but also to some extent in Southern Europe, Italy, and Southern France). *Castor beans* are also grown in different parts of the United States. The oil content of the castor bean varies between 35 and 55%, the average oil content being around 45%. The oil is extracted either unheated by pressure in hydraulic presses or by solvent extraction. The color of the oil varies from nearly colorless to yellow green; darker grades are rarely on the market (see Table XII-4). The oil is a nondrying oil which contains about 80% of the hydroxy fatty acid (ricinoleic acid, Table XII-3). Castor oil is distinguished from other oils by its high acetyl or hydroxyl value, and from other oils of comparable iodine value by its specific gravity. Unlike other oils it is miscible with al-

cohol, but is only slightly soluble in petroleum ether at room temperatures. It is much more viscous than other oils, and when completely hydrogenated has an abnormally high melting point (86–88°C.). This hydrogenated castor oil may be used for soap manufacture to raise the titer of the fatty acid mixture. A small percentage of hydrogenated castor oil will make a soap much harder. Castor oil itself is practically never used alone for the production of soap. The sodium soap is white, very hard, and transparent. This quality of castor oil soap is used when producing transparent soaps (see Ch. XXI-2). Pure castor oil soap cannot be salted-out with any practical concentration of salt or lye. Besides it has poor foaming qualities. But the presence of the hydroxy fatty acids makes it a valuable starter to accelerate saponification, especially during the cold saponification process.

Castor oil soaps dissolved in large amounts of water dissociate to a lesser degree when compared with other vegetable oil soaps. In a fat stock for a common soap, not more than 10% castor oil should usually be used, and, even in this case, a smaller amount of coconut or palm kernel oil should be used to compensate for the greater solubility in electrolyte.

According to Kranich,[63] castor oil is an excellent raw material to blend with coconut oil for the production of liquid shampoos and hand soaps, and may be used in amounts up to 25% without materially affecting the copious lather of straight coconut oil products. The addition of castor oil in this type of soaps markedly improves the rinsability of the finished products, and at the same time reduces to a marked degree the "bite," which has brought criticism to coconut oil shampoos and liquid toilet soap for soap dispensers in the past (see Chapter XXXII). Since it is a very easily saponified oil, it assists commensurably in the saponification, when blended, of other vegetable oils and fats, while a proper alkaline balance is obtained more readily in the finishing of soaps.

Castor oil may be used for a soft potash soap, but generally only in combination with other oils. The use of castor oil in the past by the manufacturer of potash soaps was not as widespread as the use of linseed oil because of its relatively high solubility as a soap. Potash soaps made from a blend of 20% castor oil with other vegetable oils have their lathering and solubility properties greatly improved in cold or tepid water.[63]

Pure potassium soap from castor oil may be produced by the cold method, in which saponification occurs very rapidly because of the emulsifying properties of the oil owing to the presence of hydroxyl groups in the triglyceride molecule and to the high viscosity of the oil. This soap, in percentages of 0.5–2%, is a valuable addition to soap flakes or toilet soaps during the milling process to impart a certain degree of plasticity and to minimize the danger of "cracking" of the soap cake (see Chapter XXIV-3).

[63] H. Kranich, *Soap*, *20*, 27–28 (March, 1944).

(13) Vegetable Fats of the Bassia Group and Similar Vegetable Fats

The chief representatives of this group of fats are cocoa butter, Mowrah or Illipé fat, Borneo butter, Shea butter, and Chinese vegetable butter. They are becoming less and less important as a raw material for soap (see Table XII-1). Cocoa butter forms the fat base for high-grade dentifrice soaps and for the soap base of tooth pastes.

Illipé, Mowrah, and the other fats are used from time to time as replacements for palm oil and to a lesser degree for palm kernel oil. It is important to analyze the fat to make sure that it does not contain too much unsaponifiable matter. In this case the percentage of the fat in the fat mixture (these fats are practically never used alone) must be lowered. The fats are easily saponifiable with NaOH of 10–12° Bé. The soaps are hard but have poor detergent and foam qualities. The soaps may be salted-out on spent lye with NaOH of 6–7° Bé or NaCl brines of 4–5.5° Bé strength. They may also be finished in niger.

(14) Palm Oil

Palm oil is obtained from the flesh of numerous varieties of the palm *Elaeis guineensis,* which grows wild in West Africa, but was later introduced and cultivated in the Dutch East Indies, Malaya, and to a small extent in other parts of East Asia, and Central and South America. The crude oil is red and the color is generally removed by oxidation with a current of air or by dichromate bleaching. The air-bleached oil very often has the disagreeable property that the color reappears in the soap pan and a reddish soap is obtained. Thus, the careful soapmaker will make a test boil with palm oil on a small scale in order to see if the color reappears. It is now known that the red color of palm oil is due chiefly to the red carotene (provitamin A) it contains. This compound is a highly unsaturated hydrocarbon having the formula $C_{40}H_{56}$. The presence of other lipochromic compounds has been reported.

If bleaching in air is properly done, the red color precipitates from the bleached fat on standing and can be removed.[64] A change may be observed during oxidation from the dark red color of the crude palm oil to a light yellow, then to an intense yellow, a dirty yellow, and finally a dirty greenish yellow. After filtration of the precipitated pitchlike oxidation products, a good grade of palm oil having a light greenish color is obtained. According to our experience, filtration is not generally necessary. The color changes mentioned in the bleaching of palm oil are not always easily followed visually, since the red color of the crude oil may appear to be unchanged for a

[64] F. Wittka, *Allgem. Oel- u. Fettztg., 35,* 187–193 (1938), through *Soap, 19,* 57–58 (August, 1938).

long time, then suddenly the color may be yellow to brownish yellow. The color change is usually accompanied by the evolution of fumes which are irritating to the eyes. After this, there is no point in carrying the oxidation further, since the lightest color possible has been reached. On further oxidation, unsaturated glycerides or fatty acids are sure to be attacked to form oxidized fatty acids. These hydroxy fatty acids have the disagreeable effect mentioned when dealing with the properties of soaps from sulfur olive oil (Ch. XVI-I, 10). The actual amount of colored material originally present is very small. The total amount of unsaponifiable matter, including the colored constituents, varies from 0.2 to 1.29%. Only a part is carotene.

It is probable that other factors, such as the impurities present and biochemical processes, have a greater influence than carotene on the various oxidation phenomena which occur in palm oil. It must be pointed out that a high percentage of unsaturated fatty acids makes it difficult to bleach palm oil by oxidation with air; oxidation of the fat molecule itself gives rise to a higher percentage of hydroxy fatty acids and nonremovable dark color. The presence of a higher percentage of free fatty acids makes oxidation bleaching with air difficult as well.

Refined palm oils for soap manufacture are very often bleached with adsorbents, so that the color remaining after air bleaching is actually removed (Ch. XIII-3, B) and does not reappear in the soap pan. Besides, no undesirable side reactions occur during adsorbent bleaching, as is very often the case during air bleaching.

Some interesting observations were made by Better[65] who demonstrated the relation of the peroxide value (see Ch. XXXVIII-14), to the actual bleaching effect of air. He demonstrated that the peroxide value rose from 7 in the crude palm oil to 167, when the bleaching effect reached its optimum (light yellow) after about 7 hrs. at 110–115; then the oil became darker brownish green and the peroxide value began to fall, probably due to the formation of hydroxy fatty acids, etc. It is important to control the bleaching process by carefully observing the point of optimum bleaching effect coinciding with the highest peroxide value and then to stop the air current and to cool the oil as quickly as possible to about 60°C. Our recent observations during practical bleaching processes on a plant scale showed that sometimes a crude palm oil with an original peroxide value of 3 is bleached when reaching a peroxide value of 35 after 5 hours at 110°C. Beyond this point the oil became considerably darker and the peroxide value fell again to 3, but dark substances were formed as the decomposition products of pigments and of the peroxides under oxidation conditions.

It is interesting to observe the fall of the peroxide value if an air-bleached crude palm oil is submitted to the usual oil refining process. For example,

[65] E. I. Better, *Allgem. Oel u. Fettztg.*, *29*, 486–491 (1932).

after neutralizing the free fatty acids (12%), the peroxide value (P.V.) fell from 35 to 20. After washing, the P.V. became 19. After bleaching with 3% bleaching earth at 80°C. *in vacuo,* the P.V. became 12.5, and, after 4 hours high vacuum deodorization at 140–150°C. with supreheated steam, the P.V. finally became 1.5.

The refined oil was practically tasteless, very light, and quite suitable for edible purposes; and, of course it had excellent properties as a soap oil. It is interesting that, when a soap was produced by the cold method from the bleached oil with a peroxide value 35 (Ch. XXXVIII-14), the fatty acids split off from this soap still showed a peroxide value of 6.5 and the fatty acids from the crude oil soap showed a value of only 1.0.

It is usually advisable to bleach crude palm oil before using it for soap boiling and not to depend on bleaching the formed soap. Only in cases where the orange color of crude palm oil is considered as desirable, *e.g.,* "figged" soft soap of the darker grades, yellow laundry and household soaps, should the crude oil be used. It was observed that soap cakes from palm oil showing the characteristic orange color were bleached to a faint yellow after exposure to the sunlight (5 days). The bleaching reached a layer of about 1 cm.; the soap below this layer was still strongly colored.

Palm oil is easily saponified. It is possible to produce good soap from palm oil alone, but a certain amount of coconut oil or palm kernel oil is advisable. The saponification is started with a NaOH solution of 10–15° Bé and finished with even stronger lyes. The soap, completely salted-out (NaOH 7.5° Bé or NaCl 5° Bé) is hard and brittle, but finished on niger it is plastic and still hard enough to form a soap cake of good consistency. In many respects palm oil soaps are similar to tallow soaps, but their detergency reaches a maximum value at a lower temperature of use. In combination with other fats and oils, palm oil may be used for the production of practically all kinds of hard sodium soaps. Potash soaps from palm oil are semi-hard and are used in the textile industry. Soaps from palm oil have an agreeable smell reminiscent of fresh hay.

(15) Coconut Oil, Palm Kernel Oil, Babassu Kernel Oil, Ucuhuba Butter, Murumuru Palm Kernel Oil

The two main representatives of this group of vegetable fats are coconut oil and palm kernel oil. Coconut oil is obtained from the kernels of the nuts of the palm *Cocos nucifera,* which grows along the coasts of Ceylon, Java, Sumatra, the Philippines, South Sea Islands, and East and West Africa.

The next important oil of this group is palm kernel oil, obtained from the kernels of the same fruit from which flesh palm oil is obtained. The oil content of the kernels ranges from 49 to 53%, which is obtained either by pres-

sure or by solvent extraction. Characteristics of coconut, palm kernel, and the other oils are given in Table XII-4.

It is important to mention that murumuru oil produced in South America has found more and more use in the United States as a raw material for soaps. Palm kernel oil, and the other oils mentioned, belong to the group of fats with a high percentage of low molecular fatty acids which form quick lathering soaps. They are thus practically indispensable, if a hard soap with good properties in every respect is to be produced.

Coconut, palm kernel, and the other oils in this group are each saponified with strong lyes (NaOH of *ca.* 38° Bé) by the cold method. If they are saponified by boiling with lye, lower concentrations (*e.g.*, 15° Bé) are suitable. The soaps of palm kernel oil can be salted-out only with very highly concentrated salt solutions (19° Bé NaOH or 16.6° Bé NaCl solutions). Coconut oil soap is salted-out with electrolyte solutions of even higher concentrations (NaOH 24° Bé or NaCl *ca.* 20° Bé). The soaps from these oils are very hard even if the soaps were produced by the cold method, where the glycerine remains in the soap. They have excellent foaming qualities, but the soaps produced from fats of this group alone have a certain rough effect on the skin (see Ch. XXXII). As the soaps are only salted-out with high concentrated solutions of sodium chloride, they may be filled to a large extent with common salt to give soaps with a very high yield (500% and more). For this reason, the soaps of this group of fats have foaming and detergent qualities even in sea water.

Generally speaking, coconut oil, among the whole group of low molecular fats, is the most valuable fat raw material for the soapmaker. In soft potash soaps a certain amount of coconut or palm kernel oil may be used especially for "silver" soaps to enhance foaming properties. For the production of liquid soaps, shampoos, etc., the fats of this group, especially coconut oil, are indispensable, but as already mentioned pure coconut oil soaps have a certain "bite" on the skin. A certain amount of other oils—especially castor oil—compensates for this effect to a large extent. Coconut oils from the refining by-products of the edible coconut oil industry, soapstock, etc., usually show a higher iodine value, which means that they have a higher percentage of unsaturated fatty acids. According to Wittka,[66] this is because the coconut contains two slightly different kinds of oils: one the common coconut oil from the flesh of the nut and the other from the thin brown layer which covers the kernel. The latter oil has a higher iodine value (about 39) and is more subject to splitting. The fatty acids of the soapstock have a higher percentage of the fatty acids of this oil. Thus, coconut fatty acids of the soapstock usually have a higher iodine value than the fatty acids of the refined oil; they

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[66] F. Wittka, *Verderben der Seifen*, Barth, Leipzig, 1939 (lithoprinted by Edwards Bros., Ann Arbor) 98–100.

may be used for the production of common household soap, but should be used only in small percentages for high-grade toilet soaps.

Soaps from palm kernel oil have a somewhat darker color than those from coconut oil; perfumes in soaps of palm kernel oil are very often not as persistent as in coconut oil soaps. Although this fact is still not explained, Wittka makes the easily oxidizable unsaponifiable matter responsible for this disadvantage.

It is not accidental that the chapter on this group of fats with a high percentage of low molecular fatty acids is relatively short. These fats are so important that they are dealt with in practically every chapter on the actual soap manufacturing processes, so that it would be an unnecessary repetition if more details were given in this introductory part on fat raw materials.

(II) ANIMAL OILS AND FATS
(1) Lard and Related Fats

Lard is obtained by rendering the fat tissues of pigs. The highest grades are used mainly for edible purposes: the lower, inedible grades are finding their way into the soap pan. Lard obtained from the kidneys and back by treatment with water in autoclaves at temperatures above 100°C., is termed "leaf lard." The next grade, "choice lard," is obtained when the hot rendering process is carried out by agitating in open kettles and heating with indirect steam. A still lower grade of edible lard, "prime steam lard," results from autoclaving the fatty tissues of other parts of the pig than the kidney and back, with the exception of other intestinal organs. In the United States, most modern plants manufacture only prime steam lard, and comparatively small amounts of leaf lard. White but inedible lard is often termed "white grease" and is quite similar to lard though it may have a free fatty acid content up to 12%.

The various lards thus produced vary in consistency and composition according to the part of the animal from which they emanate. Lard oil and lard stearine are prepared by chilling slightly and pressing. These products are also used in the soap industry; lard stearine especially is a valuable raw material for high-grade toilet soaps. Furthermore, the intestines and other parts of the animals which do not yield edible lard are separately rendered in autoclave digesters and give yellow or brown grease having a free fatty acid content of 12–25% or higher. Low-grade stocks are also frequently designated collectively as "rendered pork fat." It is evident that the lower grade of pork fat can be used only for lower grade soaps. The higher grades of lard are valuable raw materials for high-grade toilet soaps. Lard is not easily saponified. Only dilute lyes of 7–9° Bé can be used to start saponification, the process being finished with more concentrated lyes of 12–16 Bé.

Lard soap finished on niger is somewhat softer than the very hard lard soap grained-out on spent lye. It is completely salted-out at boiling tem-

peratures with NaOH of 8° Bé. The soap is not readily soluble in water, but it has a good foam and is an asset in every fatstock for soap. Lard in combination with coconut oil gives a fine toilet soap of good quality. The potassium soaps are semi-solid and opaque.

(2) Beef and Mutton Tallow

These fats are obtained from the tissues of beef or mutton, respectively, by different methods of hot rendering. The same principle applies here as in the case of lard: the higher the temperature of rendering, the lower the grade of the fat obtained. "Only a minor proportion of the total tallow production consists of an edible fat. Inedible tallows are marketed in a large number of different grades, according to their color, free fatty acid content, and content of moisture, insoluble impurities, and unsaponifiable matter. . . . Edible tallow is classed as such because it is derived from edible materials, rather than because it conforms to definite standards of color, acidity, etc. However, edible tallow generally has a light color, similar to that of lard, and a free acid content of less than 1%. The better grades of inedible tallow do not have a free fatty acid content of more than 2–3%, but they are much darker in color than edible tallow. They are bleached without difficulty," and the better grades may generally be bleached as light as edible tallow by processing. "The poorer grades of inedible tallow are extremely dark in color, and may contain free fatty acids to the extent of 40% or more."[67]

The characteristics of different grades of tallow[67] show clearly that only the lighter grades of tallow are advisable for a high-grade soap. However, the lower grades are a valuable raw material for common household soaps. It must be pointed out that a high percentage of hydroxy fatty acids in tallow (more than 3%) has great disadvantages for the soap-boiling process. Besides the actual loss of soap (see Chapter XXXIX-8, D), fats containing hydroxy fatty acids lower the keeping quality of soap.

Highly rancid tallows have a strong odor. Very often it is possible to deodorize tallow in the soap pan by boiling for some hours with live steam (Chap. XIII-4). But as a rule light, nonrancid tallow is necessary when producing a high-grade toilet soap. Even soaps from rancid tallow which was pretreated before coming into the soap pan often show low keeping quality and have a "tallowy" odor. Such soaps are difficult to perfume.

Tallows pretreated with oxidizing bleaching agents are to be used with special precautions. Here the danger of high hydroxy fatty acid content is very great and reversal of color of the finished soap is very often observed. When questionable rendering methods are suspected, the amount of hydroxy fatty acids should always be determined (Chap. XXXIX-8, D). In order to

[67] A. E. Bailey, *Industrial Oil and Fat Products*, 2nd ed. Interscience, New York, 1951, p. 147.

ascertain the quality of a tallow, under these circumstances, this test is even more important for quality termination than is the amount of the free fatty acid. For characteristics of tallow, see Table XII-5.

Saponification of tallow is started with dilute lyes of 8–11° Bé and finished with more concentrated lyes. Tallow soap is very thick and difficult to move even with live steam in the pan. It is generally saponified in combination with the other fat stocks. Pure tallow soap is completely salted-out with NaOH of 7.5° Bé or with NaCl solution of 5° Bé. The soap is very hard and does not dissolve readily in water and has poor foaming qualities in cold water. In hot water, its foaming properties and detergency are unexcelled and the pure soap finds wide use in commercial laundries. In combination with soaps of quick lathering fats, it gives a thick homogeneous foam, with excellent warm water detergency power, ideal for toilet bar use. It is by far the most universally used raw material in the soap kettle. In the United States, approximately 80% of all fat stocks used for soap are tallow.

Tallow may also be used for the production of "hard potassium soaps," which are used in the textile industry and for the production of silver and "figged" soft soap.

(3) Some Less Important Animal Fats and Oils

(a) *Horse fat* (see Table XII-5) has properties similar to lard, and is used from time to time as a substitute for the production of soap.

(b) *Greases of different origin* which may not necessarily be obtained from hog fat are also used in the soap industry. These include:[68] *tankage grease*, a low-grade product extracted from animal wastes; *house grease*, which is the waste cooking fat from restaurants and hotels; and *garbage grease*" (see Ch. XII-2), which is recovered from city garbage. "Low-grade fats in the grease class are obtained in relatively small amounts from various other sources, such as the degreasing of hides for the manufacture of patent leather and leather upholstery, the disposition of spent tinning and terne plating oils, etc."

War conditions and fat shortages after the war have made it a necessity to look for every possible source of fat raw material. At the 110th meeting of the American Chemical Society (Fall 1946, Chicago) Buch[69] presented a paper about the possible uses of garbage as a fat source. Calculated on various Los Angeles examples, the dry solids (containing the potential value of garbage) contain 14.2–23% of protein, 33.8–41% of carbohydrates, 17.1–22% of fat, 8.45–12% of fiber, and 11.6–17.6% of ash.

Experiments were also made with grease extracted from garbage, dehydrated daily and before spoilage could occur, in a number of institutions where large numbers of people are fed. The grease yield was suitable for

[68] A. E. Bailey, *loc. cit.*, pp. 145–146.
[69] W. A. Buch, *Soap and Sanit. Chemicals, 22,* 77 (Oct. 1946).

soapmaking or for fat-splitting operations, and the oil cake meal was a useful component of mixed cattle feeds.

Grease produced from spoiled garbage is poorer in quality than that extracted from freshly dried garbage.

These greases and also fats from fallen animals are used only for very low-grade soaps, but may be split into fatty acids and glycerine. The distilled fatty acids may then form a valuable raw material for soap. Technical fatty acids must be used for soapboiling according to their characteristics. They may replace oils and fats which correspond most closely in their composition.

(c) *Neatsfoot Oil*, obtained from the feet of cattle, is relatively seldom used in the soap industry. It is a light-colored oil with a low free fatty acid content and a high percentage of unsaturated fatty acids (for characteristic, see Table XII-5). Neatsfoot oil may replace to a certain extent some of the nondrying vegetable oils such as olive oil in a fatstock for soap.

(d) *Bone Fat (Bone Grease)* is more important for the soap industry. This grease is also obtained from the feet of cattle as a by-product of glue manufacture. It is used for the lower grades of soap. It may contain lime soaps as impurities which make it rather unsuitable for soap manufacture. Usually, bone fats sold to the soap industry are pretreated with acids and/or bleaching agents in order to remove the lime soaps and to improve the color of the fat. In any case a determination of the ash will show if the amount of inorganic impurities is too high. (It should be no more than 2%.) A good grade of bone fat should contain not more than 1–2% water and 2–3% unsaponifiable matter. Even the refined grades have an unpleasant odor, but may be yellow in color (see Table XII-5). To a certain extent bone fat may replace tallow in lower grade soaps, especially if rosin is used in the fatstock, and for the manufacture of silver or "figged" soft soaps.

(III) MARINE ANIMAL OILS

The fish oils contain extra long-chain fatty acids, including C_{20} and C_{22} acids, which are in the main highly unsaturated and subject to rapid oxidation and rancidity. However, the soaps from these acids have good solubility, but lack detergent power, discolor, and have a fishy odor. Therefore, raw marine oil is not a suitable material for making any but the very lowest grades of soap. But if the oils are partially hydrogenated, say to an iodine value of 65–75 (below that for oleic acid), the great proportion of these highly unsaturated acids will have been converted to stable C_{20}, C_{22}, and C_{24} saturated acids or to isooleic acids; the latter are not subject to such rapid decomposition and rancidity. The product is a rather high-melting plastic fat material, quite suitable as a substitute for tallow in the pan charge if the following points are considered. (1) The proportion of long-chain saturated acids makes the soaps derived from them very much more insoluble

than those from tallow, so that the detergency is inferior to tallow soaps ex-
cept at temperatures 10 to 20°C. above normal laundry operations.   (2)
The very presence of these long-chain acids improves the mildness effect on
the skin due the decrease in ionization with increase in chain length.   (3)
The presence of isooleic acids, some of which will be solid, plus small amounts
of the more highly unsaturated ones will tend to give a soap which may
darken somewhat on aging and which may give a slight fishy odor to laun-
dered goods when placed under the iron.   If hydrogenation is not carried
far enough, these characteristics will be enhanced.   If hydrogenation is car-
ried much beyond the point noted, stability is improved at the expense of
detergency because of the conversion of isooleic acids to saturated ones.
These iso acids are desirable, since they are good detergents in themselves.
(4) The presence of considerable quantities of these long-chain saturated
acids and solid isooleic acids decreases the ability of the soap to hold build-
ers, such as sodium silicate, so that the addition of 10 or 20% hydrogenated
fish oils in a bar soap formula may require careful adjustment of the crutcher
formula to avoid cracking, wet spots, etc., in bar soap.   Nevertheless, fish oil
is a satisfactory raw material for soap use when it is available.   In the
United States at the present time, fish oils do not play as important a role in
soapmaking as they did in the 1930's.   The reasons for this are the limited
availability due to war and postwar conditions and the increased value of
these materials through new processing methods which makes them com-
petitors of the drying oils for many operations.   One type of processing, for
example, which decreases the unsaturation and stabilizes the oil against ran-
cidity is heat polymerization, as noted by Brocklesby.[70]

The effect of polymerization on the detergency of the soaps is to decrease
the detergent value of soaps produced from such an oil as compared with
the raw oil, but there appears to be little difference in value as the polymeriza-
tion is continued from 4 to 24 hours.   The indications of this work are that
soaps can be produced which have satisfactory detergent powers for ordinary
use, either by hydrogenation alone or by polymerization followed by hy-
drogenation.   The highly unsaturated acids that cause the recurrence of
fishy odor in soaps are removed by these processes by saturating the double
bonds.

Another important development is the use of fat-splitting processes, and
distillation of fatty acids (see Ch. XIV-1, 2) to produce marine oil fatty acids
of high quality for the soap industry.   Here, what was pointed out in con-
nection with distilled fatty acids from different greases also applies: the fatty
acids must be analyzed to ascertain their characteristics and they may then be
used to replace in the fatstock those fats and oils to which the characteristics

[70] H. N. Brocklesby, ed., *The Chemistry and Technology of Marine Animal Oils with
Particular Reference to Those of Canada*, Ottawa, 1941, pp. 356–359.

most closely correspond. The characteristics of some marine animal oils suitable for soap manufacture are given in Table XII-5.

(IV) RAW MATERIAL FROM WOOD

(1) Rosin

A very important raw material for soap manufacture is rosin. This material is in fact not a fat or an oil, nor a genuine fatty acid in the chemical sense, but for the soap industry it may be dealt with as a fatty acid. Rosin is composed of about 90% rosin acids and 10% nonacids. The latter consists of hydrocarbons, high-molelular secondary alcohols, and esters. The acid portion consists of abietic, *l*-pimaric, *d*-pimaric, and other rosin acids of uncertain structure and properties. Contrary to general belief, abietic acid represents only a portion of the total acids in rosin, and may be present in any given sample from 0 to about 35%, depending upon the history of the rosin. To give an idea of the complexity of the main constituents of rosin several proposed structural formulas for two main constituents are presented.[73a] In contrast to fatty acids, these acids have an aromatic (ring) structure, whereas the fatty acids have an aliphatic (chain) structure.

H_3C $COOH$

H_2C CH_3 CH_3

Abietic acid

H_3C $COOH$

H_2C CH_3 CH_2
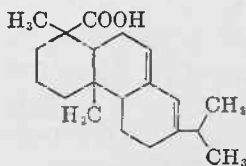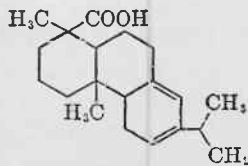
l-Pimaric acid

Rosin is contained in the exudation of the *Pinus* species, which includes: *P. palustris, P. maritima, P. pinaster, P. laricio,* and *P. taeda.* The first mentioned is the source of American rosin, and the second provides the French grade. Resins from *P. insularis, P. caribaea, P. insignis, P. pithyusa,* and *P. sylvestris* have been examined.[71]. Apart from America and France, rosin is obtained from Spain, Portugal, Greece, China, and Mexico.

The oleoresin is collected in open cups, which are emptied from time to time. It may be contaminated with wood chips, bark, leaves, dust, insects, and rain water.[72] When the oleoresin is first exuded, it is a clear viscous solution of rosin in turpentine. Due to subsequent crystallization and loss of volatile constituents the product collected becomes opaque and very viscous.

[73a] P. Karrer, *Organic Chemistry*, Elsevier, 1946, p. 692.

[71] E. F. Kurth and E. C. Sherrard, *Ind. Eng. Chem.*, 24, 1179 (1932). E. F. Kurth, *ibid.*, 25, 192 (1933). S. S. Tanchico, *Philippine J. Sci.*, 47, 481 (1932); 48, 1 (1933), Arbusov, *J. Applied Chem. U. S. S. R.*, 5, 787 (1932).

[72] Vezes and Dupont, *Résenses et Térébenthines*, Paris, 1924, p. 98.

Smith[73] estimates that as much as 8% of water may also be present. About 75% of the oleoresin is rosin. This is obtained by subjecting the oleoresin to distillation. The raw oleoresin may be purified before distillation by skimming from the surface of the molten oleoresin the lighter material, such as bark and wood chips, which float on the surface of the molten rosin. As already pointed out, the oleoresin consists of rosin in turpentine; the latter is distilled off with the assistance of steam, sometimes under vacuum. The rosin from living trees is called *gum rosin*. The rosin thus obtained still contains impurities and may be strained at elevated temperature (about 150°C.) through sieves and cotton batting to remove solid impurities. Other methods of cleansing rosin from dirt consist in dissolving the rosin in a solvent, filtering the solution, and distilling off the solvent.[74] Rosin may be extracted from raw wood by solvent extraction; the rosin obtained from the stumps or top wood of the pine tree is called *wood rosin*. Usually, the solvent used is naphtha, but water-miscible aliphatic solvents are also used in some special patented processes. The miscella is recovered from the wood residue and evaporated.

Many methods have been proposed for refining rosin. One process uses bleaching earth to bleach a solution of rosin in a solvent; another uses a kind of selective solvent process with naphtha and furfural as the selective agents (U. S. Patent 2,094,503). Chemical purification is also used in some processes (*e.g.*, hydroxyalkylamine, according to U. S. Patent 1,995,600). A hydrocarbon solution of rosin is washed with a hydroxyalkylamine. Alkylamine hydroxyabietate is precipitated and the rosin is obtained from the clear solution by evaporation. According to U. S. Patent 1,957,788, rosin is treated with a halogen at 150–350°C.

An important step was to refine rosin by catalytic hydrogenation with hydrogen. *Staybelite* (Hercules Powder Company), produced by one of these patented processes (U. S. Patent 2,113,808), is a very important raw material for the soap industry. This process—the Humphrey process—works under hydrogen pressure of 200–15,000 p.s.i. and at a temperature of 275–325°C. in the presence of an active base metal catalyst for a period ranging from 12 minutes to 3 hours. By this method the rosin may be saturated to at least 50% with hydrogen.[75]

Grades of rosin vary considerably in color. Standards issued by the U. S. Department of Agriculture are designated by letters. Thus, the darkest grades occur in the range from A to F, with the palest grades from N to X. A good series for adoption as color standards would include samples of D, E, F, G, H, I, K, M, N, WG, and WW, which last is sometimes described as water-white grade. Sometimes, rosin is sold under the designation "EP."

[73] Smith, *Ind. Eng. Chem.*, 28, 408 (1936).

[74] H. W. Chatfield, *Varnish Constituents*, Interscience, New York, 1944, pp. 76–77.

[75] *Roger's Manual of Industrial Chemistry*, 6th ed., C. C. Furnas, ed., Van Nostrand, New York, 1942, p. 695.

TABLE XVI-3

Typical Analysis of Rosins[76]

Property	Regular WG Wood	Hydro-genated[a]	Dehydro-genated (dispropor-tionated)[b]	Polymer-ized[c]
Acid number	166	162	160	150
Saponification number	172	167	170	160
Unsaponifiable matter	6.0%	9.0%	8.0%	7.0%
Softening point (Hercules drop method)	181°F.	168°F.	177°F.	214°F.
Abietic-type acid content	53%	3%	Nil	
Density	1.067	1.045	1.070	1.073
Color—U. S. rosin standard	WG	X+	X+	WG–WW
Oxygen absorption in 170 hrs. at 300 p.s.i. oxygen pressure and 25°C.	10.5%	Nil	0.06%	0.8

[a] Staybelite grade.   [b] Resin 731 grade.   [c] Poly-pale grade.

In the French system of grading the letter "A" is included in the description. Thus, the greater the number of A's used, the paler the grades. The chemical and physical properties of some typical rosins are outlined in Tables XVI-3 and -4.[76] Their theoretical soap yields are shown in Table XVI-5.[76]

TABLE XVI-4

Titer of Fatty Acids–Rosin Mixtures[76]

Mixture	Titer values, °C.
White tallow fatty acids alone	45.5
White tallow fatty acids with poly-pale (WG wood) resin (50–50)	38.8
White tallow fatty acids with K wood rosin (50–50)	34.2

TABLE XVI-5

Theoretical Soap Yields[76]

Soapstocks used	Lbs. soap per 100 lbs. soapstock	
	A (an-hydrous)	B (with 31% water)[a]
White tallow	103.5	150.2
Brown tallow	104.4	151.3
Coconut oil	104.4	151.3
"White base"[b]	103.7	150.3
"Brown base"[c]	104.4	151.3
N wood rosin	105.4	152.7
H gum rosin	105.4	152.7
N gum rosin	105.1	152.3
Hydrogenated Staybelite grade	104.9	152.0

[a] Water content of a commercial laundry soap.
[b] 75% white tallow, 25% Cochin coconut oil.
[c] 75% brown tallow, 25% Cochin coconut oil.

[76] *Rosin: Its Place in Soap*, Hercules Powder Co., Wilmington, 1943.

Pure sodium soaps from rosin are somewhat soft and sticky and, depending on the color of the rosin, either yellow or brown. The soaps are easily soluble and are quick lathering. They are completely salted-out (at boiling temperature) with NaOH of 9° Bé or NaCl of 7° Bé. Rosin is practically never used alone, in combination with other fats; however, it is a very valuable raw material for household and even light-colored toilet soap as well as for soft soaps, especially textile soaps. The pure potash soaps from rosin are somewhat soft, but have excellent lathering and detergent properties. Thus, also for soft potash soap, rosin is used in combination with other fats and oils.

During World War II and even after the war the problem of replacement of coconut oil became very important. Here, rosin plays an important role.[79] Comparison of sodium rosinate with the soaps of individual fatty acids indicated that sodium rosinate resembles sodium laurate more than the soaps of

TABLE XVI-6

LATHER STABILITY[a] OF SOAPS CONTAINING 25% ROSIN OR MODIFIED ROSIN, 36% MOISTURE BASIS, TEMPERATURE 120°F.[80]

	Height of lather, mm.			
	In soft water[b]		In hard water[c]	
	Immediate	After 15 min.	Immediate	After 15 min.
Tallow soap, no rosin (control)	200	210	200	185
N wood rosin	225	220	210	200
Hydrogenated rosin	235	235	220	215
Dehydrogenated (disproportionated) rosin	230	225	225	215

[a] Lather properties were tested according to the Ross and Miles method (see Chapter XXX).
[b] Soft water: 50 p.p.m. CaCO$_3$; soap concentration 0.25%, calculated on basis of soaps containing 36% water.
[c] Hard water: 300 p.p.m. CaCO$_3$; soap concentration 0.50%, calculated on basis of soaps containing 36% water.

the other fatty acids. In view of the similarity of sodium laurate and sodium rosinate, it appeared that rosin might be used to replace part of the coconut oil used in many soap products. Rosin soap should be considered as a material that has to be blended with other soaps. Proper blending of rosin soap with fatty acid soaps yields quality products.

In general, the addition of sodium rosinate to a fatty acid soap increases the solubility of the soap, softens the soap to some extent, increases the lathering properties of difficultly soluble soaps (Table XVI-6),[80] and of course affects the color. Light yellow soap flakes as well as light yellow bar soap can be made containing as much as 20% of rosin. If the rosin is prop-

[79] *Perfumery and Essential Oil Record*, 33, 260–262 (1942).
[80] B. S. Van Zile and J. N. Borglin, *Oil and Soap*, 22, 331–334 (1946).

erly stabilized, either catalytically or by hydrogenation, it contributes little or no color to soap products. In hard water sections, a tallow soap containing only 5% coconut oil would not produce a good lather. Addition of rosin helps to increase solubility in hard water and to give a better and quicker lather.

5–40% of rosin in the fatstock is quite feasible, especially if light-colored rosin is used. Borglin[81] elucidates, by a carefully conducted series of experiments in collaboration with Van Zile, the special advantages of modified rosins (hydrogenated and "dispropor-dehydrogenated" types) for the soap industry: (1) Enhanced wetting action of tallow-base soaps. (Coconut oil soap detracts from the wetting action, but not from the general detergent effect of the soap. (2) Modified rosin seems to impart bacteriostatic and bactericidal action not possessed by tallow-base soaps. (3) Reduced skin irritation under test conditions. (4) No decrease in detergent or sudsing action. (5) Decreased dust in spray-dried soaps. (6) Modified rosins, unlike ordinary gum and wood rosin, can be used in light-colored toilet, laundry, flake, and spray-dried soap with no material increase in color, when used in amounts allowed by present specifications. (7) Dehydrogenated rosin soap solutions are of low viscosity and, therefore, indicated for use in liquid soap preparations. (8) In limited amounts, they are suitable replacements for coconut oil or tallow, thus increasing the available supply of soapmaking raw materials and simultaneously imparting desirable properties not characteristic of tallow or coconut oil soaps. Indications are that these desirable properties are also imparted to soaps prepared when using these rosins with other soapstocks.

5 to 30% modified rosins in conjunction with tallow were the fatstocks for the soaps used in the experiments, from which the above conclusions were drawn.

As already pointed out, rosin behaves like a fatty acid during the soap-boiling process. It is easily saponified even with sodium carbonate. Since it yields no glycerine, it is usually added to the already saponified fatstock in one of the last changes after most of the glycerine has been removed. In this case the main soap mass in the pan is made strongly alkaline, and during the process of adding the rosin in lumps enough alkali must be added to saponify the rosin and to keep the boiling soap "open." Usually it is advisable to saponify rosin separately in a smaller pan, wash the soap, and then pump the rosin soap into the main soap pan.

The advantages of the latter process are that sodium carbonate, which is somewhat cheaper than caustic soda, may be used for saponification. Besides it is possible to salt-out the rosin soap separately, thus purifying it. The spent lye from the separately saponified rosin, if low in alkali, may be dis-

81 J. N. Borglin, *Soap*, 22, 43–46 (June, 1946).

carded. The rosin soap, either purified by salting-out or simply saponified, is then pumped to the main soap mass in the pan and the whole mass is boiled thoroughly to insure that the rosin soap is evenly incorporated. The whole soap mass may then be salted-out again, and the spent lye, if poor in glycerine and alkali, discarded as well. It must be pointed out that laundry and household soaps with higher percentages of rosin are especially suited to be "built up" with soap builders to increase their detergent action.

For the manufacture of powdered soaps with a relatively high fatty acid content (over 30%), common grades of rosin are to be used cautiously in the fat charge, since rosin tends to make the powdered soap somewhat tacky.

(2) Tall Oil

Tall oil is a rosin product known also as *Tallol* or liquid rosin. It is a by-product of the paper pulp industry using the sulfite process, and is obtained by hydrolysis of soaps of the alkaline waste liquors. It may be a tarry viscous liquid with a strong odor, but its color and smell vary, especially if it has been subjected to refining.[82, 82a] It is beyond the scope of this book to go into the details of the many refining processes that are used to purify the dark and odorous crude tall oil. Some processes are very similar to the refining processes for rosin (see above). Selective solvent purification, bleaching with bleaching earth, and hydrogenation are methods to purify the crude oil. Sometimes the rosin acids are removed by crystallization at low temperatures. Deodorization processes are often employed similar to those usually used for oils and fats. In recent times tall oil has gained more and more importance for the soap industry. It is not only extensively used for the production of textile and other specialty soaps, but also for common household soaps.

A new kind of tall oil may soon be available for industrial use which is obtained by direct extraction of thin sheets or saw dust of pine wood (*e.g.*, with benzene 50°C.). The composition of the benzene-extracted oil is given refining. It is to be expected that such directly extracted tall oils will be valuable raw material for the soap industry as well.

In the United States, grades of refined tall oils mainly from waste liquors are used in soap manufacture. Analytical data are given in Table XVI-8.[84]

According to Wheeler,[85] tall oil consists of 45–50% rosin acids, 45–50% fatty acids and 5–10% unsaponifiable matter. The fatty acids consist mainly in Table XVI-7.[83] The products thus obtained are less acidic and require no

[82] H. W. Chatfield, *Varnish Constituents*, Leonard Hill, London; Interscience, New York, 1944.

[82a] J. P. Casey, *Pulp and Paper*, Interscience, New York, Vol. I, pp. 174–176.

[83] A. B. Andersen, *Ind. Eng. Chem.*, 38, 760 (1946).

[84] R. Hastings, *Am. Dyestuff Reptr.*, 33, 25–26 (1944).

[85] D. H. Wheeler, *Org. Finishing*, 9, No. 10, 17 (1948).

TABLE XVI-7

Per Cent by Weight of Extractives[83]

	Heartwood	Sapwood
H_2O + ether-insoluble	0.0	0.0
H_2O-soluble	0.6	1.0
Resin acids	58.5	29.8
Fatty acids	12.1	42.8
Volatile	5.6	3.0
Esters	12.0	13.0
Unsaponifiable	11.1	10.2
Extractives, % by wt. of moisture-free wood	10.0	3.1

of oleic and linoleic acids with small amounts of palmitic acid. The rosin acids are similar to ordinary rosin.

Pure sodium soaps from tall oil alone are dark brown or light yellow, soft, and tacky, and have properties similar to rosin soaps. Potassium soaps from tall oil are very soft. Tall oil is usually not used for hard soap in amounts greater than 25% of the fatstock. But with alkailne soapbuilders even hard soaps with higher percentages of tall oil may be produced. Tall oil has many advantages for the production of liquid soaps, since potash tall oil soaps are soluble in water in high percentages without gelation.

The use of tall oil for the soap industry was outlined in a paper by Hastings, Pollack and Wafer,[86] and many practical examples given. The following methods for the preparation of high concentration paste or liquid soaps from tall oil alone are described as follows:

(1) Heat the tall oil to about 175°F. (79–80°C.) until any crystals have dissolved.

(2) Heat requisite amount of 30% caustic solution (see step 2 under preparation of liquid soaps below) to 175°F. Either sodium or potassium hydroxide or their mixtures may be used.

(3) Slowly pour the hot caustic solution into the hot tall oil with slow agitation.

TABLE XVI-8[84]

Properties	Tall oil	
	Crude	Refined
Acid number	160–170	170–180
Saponification number	165–175	170–185
Rosin-acids number	80–90	63–71
Wijs iodine number	140–150	—
Ash, %	< 0.4	< 0.1
Fatty acids (chiefly oleic), %	45–50	55–60
Rosin acids (calc. as abietic), %	42–48	34–38
Sterols, higher alcohols, etc., %	6–9	6–10

[86] R. Hastings, A. Pollack, and I. M. Wafer, *Soap*, *19*, No. 5, 24–27, 70 (1943).

Mechanical agitators should operate at slow speeds and should be well submerged to prevent entrainment of air.

(4) Add enough water at 175°F. to bring the soap to the desired water content. If no water is added, using caustic soda, an 80% soap results; using caustic potash, a 74% soap.

(5) Continue agitation until uniform.

To prepare a liquid soda or potash soap of tall oil the following typical procedure is recommended:

(1) Heat the tall oil with agitation in a tank or other suitable container to 150–175°F. (66–80°C.) until any crystals present have dissolved. This operation will require only 5–10 minutes heating after reaching 150°F.

(2) For each 1,000 pounds of tall oil used, weigh out 125 pounds of caustic soda or 175 pounds of caustic potash (100% basis).

(3) Dissolve the caustic soda or potash in the total amount of water used. The amount of water used will depend on the desired soap content of the finished soap solution.

(4) Slowly add the alkali solution to the tall oil with agitation.

(5) Continue the agitation until the mixture becomes uniform.

By using the above proportions of tall oil and alkali, the soap formed will not contain appreciable amounts of free alkali. If desired, soapbuilders and excess alkali may be added. The amount used is best determined by trial, but in general it will not differ materially from the amounts of excess alkali and builders used with other soaps. In the United States, liquid and paste soaps of tall oil have proved effective for scouring wool, rayon, and cotton linters, for the degumming of silk and depitching of rayon pulps. In European literature, Henk[87] states that tall oil soap can be used for the most varied textile requirements, including scouring raw wool, washing white woolens, washing cotton, dyeing, desizing, and degumming of silk.

As already pointed out, hard soaps cannot be prepared from tall oil alone by any graining process. However, hard soaps can be obtained by drying processes or by adding soapbuilders such as soda ash. For example, German Patent 482,458 claims a process for producing a hard soap from tall oil soap paste in which the paste is kneaded with 2 to 15% of calcined soda. In carrying out this invention, 6500 kg. of tall oil is neutralized with 33° Bé caustic soda, whereby 10,000 kg. of soap paste is obtained. 800 kg. of calcined soda ash is added and kneaded into the soap. The kneaded mass is sent over a cooling roll, from which it is transferred to a packaging machine. In this machine the mass is kneaded once more and pressed into cakes of about 0.5 kg. The soap cakes coming out of the machines assume a hard, firm form after a short time.

Tall oil mixed with other fats is used in the preparation of hard soaps.

[87] H. J. Henk, *Seifensieder Ztg.*, 67, 22 (1940).

As a typical illustration of a hard soap containing tall oil, Straus[88] uses the following soapstock:

	Parts
Hard fat	50
Tall oil	20
Coconut fatty acids	20
Peanut oil fatty acids	10

This soapstock, when saponified with caustic soda and salted-out, gave a light brown soap.

Straus also states that the following soapstock is used for the preparation of a toilet soap.

	Per cent
Hard fat	53.7
Tallow	29
Rosin	5.2
Refined tall oil	12.1

For special cleaning soaps (auto soap, scrub soaps, dry cleaning, metal cleaner soap, etc.) even crude grades of tall oil may be used. The odor of tall oil in these cases is not a serious handicap and may be masked with pine odors. When purchasing a tall oil for normal soap purposes the amount of unsaponifiable fatty matter is of great importance; more than 8% makes the oil less suitable for soaps, except for the production of some special cleaners.

(V) GENERAL REMARKS ON THE CHOICE OF A FATSTOCK

Fatstocks must be chosen carefully, especially for a high-grade toilet soap. The first condition is that the fats and oils be of high purity and/or refined as prescribed in Chapter XIII. No rancid fats or fatty acids should be used and none or only traces of mucilaginous substances should be present in the fatstock. Very important is the absence of hydroxy fatty acids (see Chapters XVI-I, 14, XVI-II, 2, and XXXIX-8, D). As a matter of fact, conditions for the choice of a fatstock are the severest for light-colored toilet soaps and less strict for laundry soaps of the yellow type.

In a publication by Wittka,[89] an attempt was made to classify fats into five groups, according to the degree of rancidity of soaps prepared from them:

Group 1. Fats yielding hard soaps—include tallow, lard and hardened fats.
Group 2. Fats yielding soft soaps which are relatively stable and are modified only to a slight extent when kept in the air—include the liquid nondrying fatty oils.

[88] R. Strauss, *Deut. Parfumerie Ztg.*, **25**, 406–409 (1939).
[89] F. Wittka, *Seifensieder Ztg.*, **57**, 773–775 (1930).

Group 3. Fats yielding very soft soaps which readily undergo modification in the air, and when kept in storage are liquid fats belonging to the group of drying and semi-drying oils.

Group 4. Fats of the coconut oil group—contain fatty acids of low acids of low molecular weight.

Group 5. Resins which differ fundamentally from fatty acids in chemical structure, but resemble the latter in forming colloidal solutions of salts in water.

So divergent are these five groups in properties that responsibility for rancidification of soaps can be ascribed to them in different directions. And not merely to the type of rancidity, but also the speed at which the change proceeds from group to group.

In the case of *Group 1,* Wittka goes on to point out that the fatty acids of these fats are not very sensitive to oxygen, and soaps prepared from these fats are correspondingly stable. Members of *Group 2* show a greater tendency to oxidize (higher iodine value) and may thus cause mottling in soaps, especially if metallic catalysts are present. Soaps prepared from fats of *Group 3* possess a still higher iodine value, and are still more prone to oxidation and consequently to rancidification and mottling. *Group 4,* it is pointed out, yield soaps with the least tendency of all to develop rancidity. Fats of *Group 5* resemble those of Group 2, but do not develop unpleasant odors.

Wittka distinguishes between two types of rancidity: rancidity by oxidation of the fatty acids, and rancidity after secondary splitting accompanied by liberation of the lower fatty acids. In a particular case, both factors may come into play. Among soaps becoming rancid as a result of oxidation are those prepared by fats belonging to Groups 1, 2, and 3.

One of the present authors raised objections to Wittka's classification. In a short note the following point was made:[90] semidrying and drying oils do not necessarily cause rancidity or yellow spots in all cases and in all soaps. As is well known, sunflower oil—a drying oil—is used in Soviet Russia not only for making curd and Eschweg soaps, but also for toilet soap bases. Yet no complaints are forthcoming from that country, and J. Davidsohn frequently received milled toilet soaps from Russia which were excellent with respect to color, and were quite free from rancidity. (Rancidity and its prevention are discussed in Chapter XXXI.)

After having dealt with the fatstock with regard to the keeping quality of soap,[91] we have now to deal with another aspect of building up a suitable fatstock for hard soaps. In Table XII-7 details were given on the properties of soaps obtained from different fats and oils. It requires the skill and experience of a soapmaker to compound the fatstock in such a way as to produce a soap with the necessary qualities: hardness of cake, easy solubility in water of normal temperature, good foaming and detergent quality. All these quali-

[90] J. Davidsohn, *Seifensieder Ztg.*, 57, 794 (1930). E. J. Better, *Allgem. Oel u. Fettztg.*, 28, 380 (1931).

[91] J. Davidsohn and A. Davidsohn, *Soap Perfumery & Cosmetics*, 9, 702–706 (1936).

ties make the "ideal" soap. It is practically impossible to combine all into one soap, but the soapmaker attempts to achieve the best possible product under existing conditions.

Once, the titer of a soap fat was considered as the most important analytical value for the soapmaker, and in fact the titer has a very important bearing on the behavior of the soap (see Table XVI-9). But foaming quality and detergent effect naturally do not correspond to the titer alone. For example, coconut oil has a low titer, gives a hard soap of easy solubility and fast foaming action. Tallow has a high titer, gives a hard soap, only soluble slowly in warm water, with little foaming action. Oleic acid has a low titer, gives a soft, fast dissolving soap with poor foaming quality. Thus another factor was developed by Webb[92]. The I.N.S. factor, which is the difference between the saponification value and the iodine value of the oil (saponification value – iodine number = I.N.S. factor). With increase of I.N.S. factor,

TABLE XVI-9

TITER OF FATTY ACID

		Fatty acid Titer, °C.	Appearance of turbidity in soap solution, °C.
Lauric	$C_{11}H_{2}COOH$	44	40–45
Myristic	$C_{13}H_{27}COOH$	54	50–55
Palmitic	$C_{15}H_{31}COOH$	62	60–65
Stearic	$C_{17}H_{35}COOH$	71	65–70
Arachidic	$C_{19}H_{39}COOH$	77	75–80
Oleic	$C_{17}H_{33}COOH$	14	20–30

the soaps from the oils are harder, less soluble, less prone to rancidity, and have better color, but are poorer in respect to detergent and lathering powers. Estimation of the mean I.N.S. factor of a blend of oils is supposed to enable one to determine in advance the type of soap produced on saponification. The I.N.S. values range from 250 for coconut oil to 15 for linseed oil.

The soap solubility ratio (S.S.R.) is the ratio of the I.N.S. factors of the mixture of oils to the sum of the I.N.S. factors of those oils in the mixture with a factor greater than 130 (excluding palm kernel and coconut oils); high S.S.R. values indicate good lathering qualities and solubility. We cannot quite agree with Webb that these factors are reliable for the evaluation of the properties of a soap from the above mentioned analytical figures of the fats and oils used.

In many respects this is not so important either. With the knowledge of the qualities of pure soaps made from individual fats and oils it is not too difficult to build up a suitable soap base. If a soap manufacturer is very careful, he will make an experimental boil on a small scale before deciding on every new soap base he intends to use.

[92] T. E. Webb, *Modern Soap and Glycerine Manufacture.* Davis Bros., London, 1927.
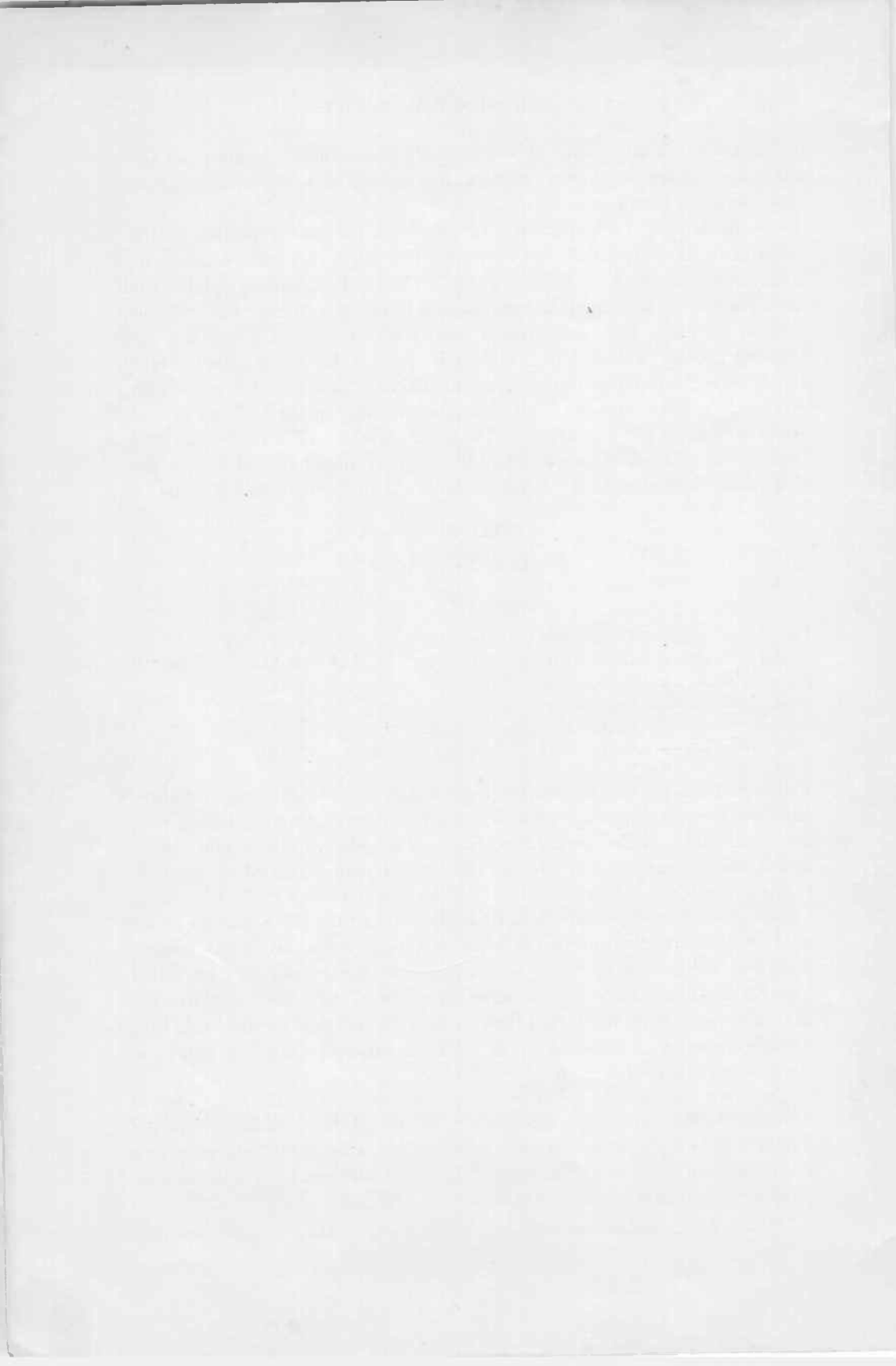
PART C

Practical Soap-Boiling Processes
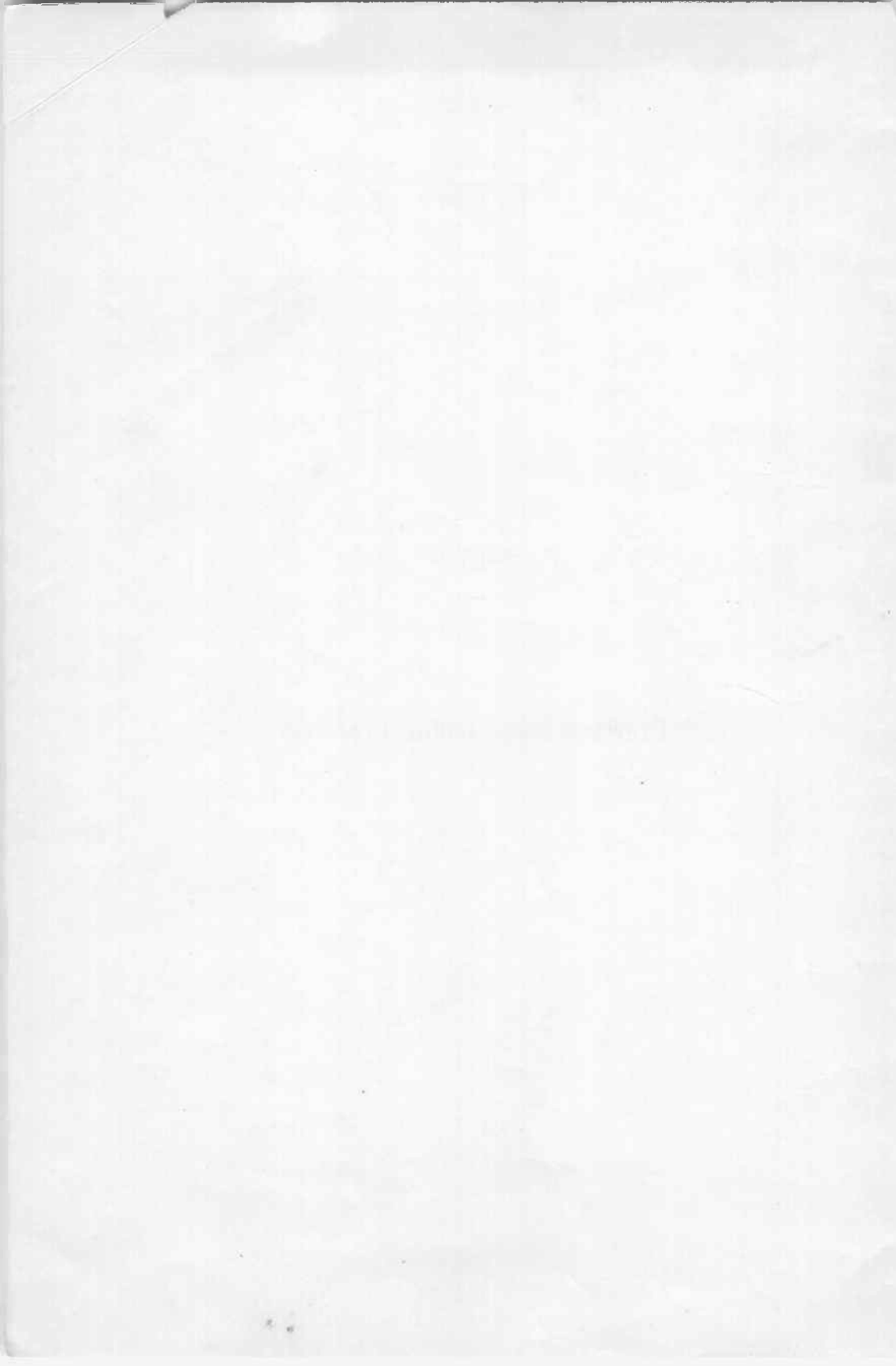
Introduction

Briefly, the objects of the soapmaker are: (*a*) To choose a properly composed fat mixture suiting the special use and purpose of the soap to be produced, and its conversion into completely finished soap. (*b*) To employ a method which would enable him to obtain the greatest possible yield of marketable products from a given volume of fat that is commensurate with a minimum size of plant. (*c*) To retain full control over the pan contents during the process, and over the quality of the final product and its composition in regard to fat, water, electrolytes, free alkali, glycerine, and its content of unsaponified fat. (*d*) To recover a maximum amount of the glycerine from the saponified fat contained in a minimum amount of spent lye, producing in this way as highly concentrated glycerine solutions as possible.

Because of the great variety of soap products now on the market, a correspondingly large number of practical soapmaking methods are in use, which are classified as follows:

(*1*) *The cold-made process.* Calculated amounts of fat and concentrated lye are intimately mixed until saponification sets in and is completed within a few hours. This process is generally used when the fat charge contains coconut, palm kernel, and babassu oils exclusively, or at least large proportions of these fats. It is difficult in this case to retain perfect control over the composition of the product. It is almost impossible to provide an exact amount of the alkali to ensure that, ultimately, the product shall contain no more than the requisite small amount of free alkali and no unsaponified fat. On the contrary, accepted practice with this method is to use an insufficient amount of alkali lye and to leave some unsaponified fat in the soap. No glycerine is produced by this method, since after saponification no additional processes are used for taking it out and it therefore remains in the product. On the other hand, the yield of soap is well in hand because the fat charge is converted into a marketable product and no losses occur, as there are no byproducts like lyes or nigers with this process. Equipment cost is also at a minimum because of the quick and simple nature of the process. In this process, however, only very pure raw materials can be used because of the nonexistence of changes and washes for the elimination of impurities.

(*2*) *The half-boiled process.* It differs from the cold process only by

the detail that the ingredients are heated up to about 90°C. In this process, there is some degree of control over the composition of the product, due to the fact that at the end of the saponification the mass is sufficiently liquid to permit the addition of free fatty acids, fat, or alkali for neutralization of the mixture.*

(3) *The full-boiled process.* The fat composition is boiled with an amount of alkali solution slightly in excess of that required for exact saponification. Once complete saponification has been accomplished, the operator may follow two courses in order to obtain the finished soap:

(a) The full-boiled process may be employed to produce *unsettled* soaps. In such cases no salting-out follows the preliminary saponification and the product remains as it was at the moment of complete saponification. The only difference between this and the "half-boiled process" is that in the former case the mass is kept properly "boiling" and not just "hot." One important product of this kind of process is the soft potash soap which is produced by boiling linseed oil or a mixture of this with some other oil with caustic potash and leaving the glycerine in the saponified mass.

(b) In the second kind of process the product of saponification is separated from excess water, glycerine, alkali, and electrolytes by one or several salting-out procedures or washes. Soaps produced by this method are called *settled soaps.* There are two kinds of settled soaps: (1) the product of the process when salting-out is complete (these soaps are called *curd soap* or *soaps boiled on clear lye*), and (2) the product of "partial salting-out" (in this case the soap does not settle on a clear lye, but on a soap solution called the *niger.* These soaps are called *fitted, genuine,* or *neat soaps*). The process of settling soap on clear lye as compared with making neat soap settled on niger, gives a higher yield out of one pan batch. It will be seen, however, that the ultimate soap yields are identical in both processes. "Fitting on niger" requires somewhat more kettle space, since the kettle is occupied during a somewhat longer period only because of the necessity of reworking the nigers. It is a generally accepted fact that fitted neat soaps are superior in quality, and especially in texture, to those settled on clear lye. It is furthermore true that this process gives the fullest guarantee for the control over the ultimate composition of the final product.

* The terms *half-boiled* and *semi-boiled* are synonymous.

THE FULL–BOILED PROCESS

(1) General

This process is also described in the appendix on small-scale experimental boils. Considerable skill must be acquired by the soapmaker before he is able to conduct a large boil without running the risk of spoiling the pan contents. In present-day practice an overwhelming proportion of the total soap production is still provided by the full-boiled process and it is for this reason that we deal with the description of this method first.

A great deal of practical experience is required to carry the full-boiled process successfully through its various stages. Running in the proper fat charge, saponification, graining, finishing, fitting, and other details were handled in the past in an empirical manner. In fact, soapmaking has been, until recently, characterized less by theoretical considerations than by familiarity with the appearance which soap may assume at various stages during boiling. Exact measurement and analysis were seldom employed and it was through the senses of touch, sight, and taste that the process was controlled.

It has been shown in the theoretical part of this book and in the description of exact experimental boils in the appendix that small changes in the water and electrolyte contents in the pan cause variations in the composition of the final soap product and also in the composition of the spent lye. We have learned from the phase diagram that neat soap occupies an area and not a fixed point, that we may be able to produce neat soap corresponding in composition to any point within this area, and that this is dependent only on the condition chosen for the final settling of the soap. It is therefore natural, when armed with present-day theoretical knowledge and induced by the highly exacting technical and commercial requirements of the times, that it is no longer necessary or desirable to rely upon craftmanship only. In soap-

making, just as in any other branch of modern chemical technology, the
necessity is felt for controlling the process to the fullest possible extent by
exact measurements of all quantities involved, by analyzing the products,
and by comparing the results with those theoretically expected.

It is assumed that all quantities of raw materials and ingredients entering
the kettle have been carefully weighed and the amounts duly recorded. How-
ever, this is very seldom the case, even in modern soap factories, as in most of
them at least some of the ingredients, water and brine, for instance, are added
directly and without quantitative control. Furthermore, the water content of
the pan is very seldom known during the process, due to the fact that, by
boiling with open steam, water is constantly added by condensation and the
exact weight of the water added cannot be directly ascertained. It would,
of course, be possible to find out the true water content of the boiling mass at
any time of the boil if a water determination were made on a representative
sample of the pan content.

The shape and dimensions of the kettles and the way the ingredients, fats
and lye, are run in are of great influence on the saponification process. Fats
or alkalies, when run in too quickly or without due care for their immediate
dispersal in the kettle and subsequent intimate mixing with the pan contents,
tend to form lumps which are difficult to boil out. Variations in steam pres-
sure in the boiler house or in the regulation of the steam valve at the pan
may cause important changes in the pan condition. Too rapid a saponifica-
tion and a sudden release of reaction heat has a more serious effect in large-
scale boiling than in small-scale boiling, since the heat evolved cannot be
eliminated as quickly in the surrounding mass, and often results in the pan
boiling over.

The phenomenon of *bunching* is much more likely to occur in a large
pan than in a small one because in the former a local deficiency in caustic
may easily occur due to uneven boiling (see Chapter XVIII).

It was described in Chapter V how size and shape of the pan influence
the separation of the layers and, especially, the rate of settling of the niger
from the fitted soap mass. However, no difference is observed between the
L.L.C. when established for the same fat charge on a small or a large scale,
and thus these critical electrolyte concentrations, once determined in a small
experiment, hold good for the large-scale boils as well.

The same applies to the electrolyte concentration characteristic for a
certain grade of fit, and thus this type of information obtained by small-scale
experimentation can be carried over and utilized in the technical operation.
The rules of glycerine recovery by repeated washes or changes as studied in
laboratory boils can also be very well applied to actual practice.

From the point of view of glycerine recovery and also for the ultimate
electrolyte content of the soap, the extent of separation of the soap layers is

naturally of the greatest importance. However, this depends on a time factor, namely the rate of cooling of the soap mass in the pan (Chapter VI). It was shown that it is the size and shape of the pan which have great influence on these factors and this again demonstrates how the dimensions of the boil may change considerably the course of the process.

As a useful guide in these circumstances, the setting up of certain standards in the control of soap plant operations is advantageous. The elaboration of a *kettle plan* may serve as a further help in practical soapmaking.

(2) Use of Standards in Control of Soap Plant Operations

In order to attain the maximum technical performance it is necessary to establish a set of standards to enable the plant superintendent to control the operations in the plant processes. Peterson[1] contributes an instructive article on this subject.

Several types of soap are usually manufactured in the same factory. The soapmaker receives his directives from the management as to the kind and amount of marketable soap products to be manufactured during the running month. Knowing the kind and size of the kettles and other equipment at his disposal, he must then make his plans in order to be able to carry out the production of the various types of merchandise. When making his plans he should, however, take into consideration the general criteria expounded in the first sentence of Part C of this book.

From a thorough survey of the equipment available the following standards may be derived and set up.

(A) The Kettle Capacity Standard

In the kettle room the value of a standard for the output of a given number of kettles is twofold. First, it establishes the maximum "normal" capacity of the plant and avoids the otherwise all too frequent differences in opinion on this point. Second, when the full plant capacity is not required, economy in steam may be gained by reducing the number of kettles in active use, thus decreasing radiation losses.

In setting a standard for the capacity of a kettle room, one must determine the fair minimum number of hours required to perform all of the boiling operations, eliminating from consideration all unnecessary delays, such as excess loss of time by waiting for the delivery of materials from another department (fats, rosin, salts, caustic), failure of mechanical equipment (pumps, pipelines, valves). The minimum settling time necessary to yield kettle soap of the desired quality, the fair minimum time required to deliver the settled soap to the next operation, and, finally, the time necessary to pre-

[1] W. A. Peterson, *Oil and Soap*, *17*, 66 (1940).

pare the kettle for the next boil give a relationship between the hours available per week and the number of hours required for a complete turnover of a kettle. This relation is the normal *kettle cycle* and may be expressed as *boils per kettle per week*. Knowing the kettle equipment available, the overall weekly or monthly capacity of the kettle department may be calculated. Because the kettle cycle sometimes varies for different types of soaps, it is even more desirable to establish the capacity for each type produced.

There are other types of standards which must be taken into consideration by the plant superintendent or the soapmaker when making his kettle plan. These are the "loss of material" standards.

(B) Loss of Alkali Standards

In the soap-boiling process, one well-known source of loss is the alkali remaining in the spent lye sent to the glycerine refinery, and in waste lyes run to the sewer. Taking up first the case of spent glycerine lye, it will be seen that here a double expense is involved. Not only is the alkali lost, but acid or other chemicals must be used to neutralize it in the lye treatment operation. The excess alkali may be neutralized in the kettle by fatty acids.

An alternative is to provide for an excess of neutral fats, at the same time extending the time of boiling. But each additional hour of boiling consumes steam and cuts into the kettle output by lengthening the turnover cycle. Consequently, one has to find an economical balance between the cost of extending the time of boiling, or using fatty acids, and the cost of leaving the alkali in the spent lye. The ultimate standard will be expressed as *the maximum allowable per cent alkali in spent lye.*

Another source of alkali loss in the kettle room is in waste lyes run to the sewer from the processing of the darker fats for soap powders and resin for laundry soaps. The usual method for improving the color of these stocks is to give them one or more alkali washes. The resulting lyes are dark in color, contain little or no glycerine, and are usually discarded.

(C) The Lye-Bulk

There is a second standard necessary here to obtain complete control, namely, *the maximum allowable quantity of spent lye in relation to the fat stock saponified.* It is of no benefit to have a satisfactory value for the per cent alkali in the spent lye, only to find that the bulk of the lye is twice as large as it should be. Here the *lye-bulk* must be determined by consideration of the particular type of kettle system used (countercurrent or noncountercurrent), whether the kettles are boiled with open or closed steam, the extent to which it is desired to recover the glycerine and the capacity of lye storage space.

(D) Loss of Soap in the Lye

All lyes contain small amounts of dissolved soap normally ranging from 0.05–0.5%. As this is a direct loss, it is important to operate within the standard lye-bulk in each case; in order to avoid an excessive percentage of soap in these lyes, it is advisable to have a standard for the Baumé (or specific gravity) of the lyes before they leave the kettles in order to provide a salt content high enough to ensure a minimum percentage of dissolved soap. The *minimum standard Baumé* should be higher by one or two degrees than the point at which the soap content in the lye becomes constant when raising the salt content. In addition, it is advantageous to allow the lye to cool, settle, and skim off part of this soap before permitting them to be treated for glycerine recovery.

(E) Loss of Glycerine

As to the glycerine left in the kettle soap delivered, the standard allowable loss involves a detailed survey of whatever system is in use, after which the added cost of each additional per cent recovered can be calculated. Additional expenses may be caused by an increase in lye-bulk. The point to be emphasized is that all conditions must be considered to obtain the true balance between the additional amount of glycerine that would be recovered and the cost of getting it. The safest way is to set up two columns *System A* and *System B*, under which every component of the cost in the kettle department should be listed. Certain expenses are fixed, others vary, but by listing all of them the total cost of the operation and the total glycerine recovered under each system can be ascertained. The difference can be expressed either as the *unit cost for the additional glycerine recovered* or, as the *over-all unit cost of the glycerine recovered*. At some point, the further recovery of glycerine will be overbalanced by the additional cost, and it is necessary to standardize at the point at which a satisfactory profit is realized.

(3) The Kettle Plan

The kettle plan can be evolved only when the various standards have been established and all conditions duly considered. For conditions in which maximum glycerine recovery is indicated, the following countercurrent wash kettle plan proposed by Govan[2] serves as a very good and instructive example. It has already been pointed out in this book that the glycerine concentration in the aqueous portion of the curd is equal to the concentration in the lye. This means that the degree of glycerine recovery from each wash depends entirely on the quantity of lye removed in relation to the entangled lye which remains in the curd. A definite kettle recovery of glycerine can be obtained

[2] W. J. Govan, Jr., *Oil and Soap, 19,* 79 (1942).

by being able to regulate the weight of the "washes" in relation to the weight of the curd.   The curd, under ordinary kettle operation, will hold 35–38% of its weight of "entangled lye" (entrained or occluded lye) (compare with Chapters V and VI).

Govan uses the manometric gage (back pressure liquid level gage of the manometric or dial type) for weighing the total kettle content.   The apparatus used for weighing the washes is fully described by Wigner.[3]

The sketch in Fig. XVII-1 and description represent Govan's[2] adaptation of the apparatus.
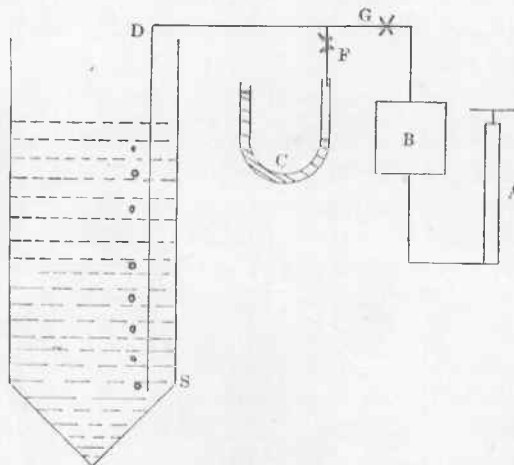
Fig. XVII-1.   Manometric gage.[2]   (A) Automobile tire pump.   (B) Compression chamber.   (C) U-tube mercury manometer, using a meter stick divided into millimeters.   (D) Two-inch pipe.   (F, G) Valves.

Valve F is closed, G is left open.   Air is pumped into the system until bubbles break through the surface of the kettle.   Valve G is closed, valve F is opened, and the difference in millimeters between the two levels of mercury in the manometer is noted.

Millimeters times *kettle factor* gives the total weight of the kettle contents above opening S of pipeline D in the bottom of the kettle.   The weight of the kettle content in the cone below opening S is to be regarded as a constant *kettle tare* and may be obtained directly or computed.   The kettle factor itself may be computed from the horizontal cross section of the kettle or may be calibrated directly by noting the manometric differential against a known weight of material pumped into the kettle.   (The factor for a kettle 15 feet in diameter is 490 lbs. for each millimeter head of mercury. The tare on the cone section below the pipe opening S for a cone 2.5 feet deep is 9,000 lbs. for lye and 6,000–7,000 lbs. for kettle soap.)   The accuracy of these weighings is independent of the condition of the material in the kettle.   It can be nonhomogeneous and at any temperature as long as fluidity is maintained.

[3] J. H. Wigner, *Soap Manufacture.   The Chemical Process*, Chemical Pub. Co., New York, 1940.

In the *operation of the kettle,* the total contents are built up to a specific weight. After the wash is run out, the curd is also weighed. The difference between the total weight of the kettle and the weight of the curd gives the weight of the lye withdrawn. The aqueous portion of the curd is estimated by deducting the known amount of dry charge from the curd. The percentage removal of free glycerine from the kettle is the ratio of wash to the total aqueous medium in the kettle.

If a kettle is oversalted, or not allowed sufficient settling time, the curd will contain more entrained lye than it should. By keeping a record, proper salt concentration in the lye, and proper settling time, we obtain what may be called an "efficient curd."

(A) SYSTEM OF WASHES

Govan[4] has reviewed the various wash systems known. We reproduce in the following pages his excellent discussion of the topic:

There are three general systems of washes used in the full-boiled method of soap-making. The main purposes of washes are to cleanse impurities and coloring matter from the soap and to recover glycerine which the fats and oils yield on saponification.

TABLE XVII-1

INDIVIDUAL WASH SYSTEM

Saponification change ⎤
Glycerine change   ⎬ ————————   Lyes to crude glycerine recovery department
Glycerine change   ⎦
Strengthening change[a] ————————   Lye to saponification change of succeeding kettle
Fitting change —————————————————   —

[a] Optional.

Individual Wash System. The earliest system of washes (see Table XVII-1) is one in which several successive fresh neutral washes are made on the same kettle for glycerine recovery. Saponification and fitting operations are carried out in the customary manner.

This system of washes is still much used where the number of kettles is limited and various grades of stock must be handled without the possibility of contaminating good soapstock by countercurrent washes from poorer soapstock.

The individual system of washes has one major drawback, production of a relatively large amount of spent soap lye compared with the amount produced in countercurrent systems. Consequently, in the individual wash system, labor, material, and steam costs for evaporating spent lye to crude glycerine are often double those in the countercurrent system (see Fig. XVII-3 below). This places the former system at an obvious economic disadvantage.

Semicountercurrent System. A second system of washes, semicountercurrent (see Table XVII-2), is a compromise between the individual system just described and a straight countercurrent system. In this system, several fresh washes of varying caustic

[4] W. J. Govan, Jr., *Oil and Soap,* **23,** 229–235 (1946) ; or *Soap, Perfumery and Cosmetics,* **20,** 157–163 (1947).

DAY OF CYCLE

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |

Lye from D   50000 Fat   Lye from D   23100 Niger

A

Change 1
79900 Curd
61400 Lye
Lye to Glyc. Dept.

Change 2
83000 Curd
83200 Lye
Lye

Change 3
97700 Curd
77200 Lye
Lye

Change 4 Fit
102000

Settle
102000

Settle
78900 Neat
23100 Niger

Settle
78900 Neat
23100 Niger
Neat to process

23100 Niger
Niger to storage

50000 Fat

B

78900 Neat
23100 Niger
Neat to process

23100 Niger
Niger to storage

Change 1
79900 Curd
61400 Lye
Lye to Glyc. Dept.

Change 2
83000 Curd
83200 Lye
Lye

Change 3
97700 Curd
77200 Lye

Change 4 Fit
102000

Settle
102000

Settle
78900 Neat
23100 Niger

23100 Niger

50000 Fat

23100 Niger

C

Settle
10200

Settle
78900 Neat
23100 Niger

78900 Neat
23100 Niger
Neat to process

23100 Niger
Niger to storage

Change 1
79900 Curd
61400 Lye
Lye to Glyc. Dept.

Change 2
83000 Curd
83200 Lye
Lye

Change 3
97700 Curd
77200 Lye
Lye

Change 4 Fit
102000

50000 Fat

23100 Niger

D

Change 3
97700 Curd
77200 Lye
Lye to A

Change 4 Fit
102000

Settle
102000

Settle
78900 Neat
23100 Niger

78900 Neat
23100 Niger
Neat to process

23100 Niger
Niger to storage

Change 1
79900 Curd
61400 Lye
Lye to Glyc. Dept.

Change 2
83200 Curd
83200 Lye
Lye to A

KETTLE

Fig. XVII-2. Countercurrent flow sheet.[4]

COUNTERCURRENT FLOWSHEET FOUR KETTLE UNIT

soda strength are drawn off the same kettle into storage tanks. These washes are later used in the saponification or "killing" change in succeeding kettles, where they are "enriched" by picking up more glycerine and where their caustic soda strength is spent in saponifying fresh fats and oils.

The semicountercurrent system has the same advantage as the individual wash system for soap plants having limited kettle facilities. A variety of soapstock can be processed with little possibility of contamination of good stock through interchange of lyes.

It has the advantage over the individual wash system of reducing the amount of spent soap lye produced by about 25%, with a proportionate reduction of operating costs in the crude glycerine plant.

Here again there are serious disadvantages in this system compared with the straight countercurrent system. Over one and one-half times the amount of spent soap lye is produced in the semicountercurrent system as in the countercurrent system. This means that labor, material, and steam costs of producing crude glycerine are about one and one-half times those in the countercurrent system.

A second disadvantage is in the extra amount of time, labor and expense consumed in running partly spent lyes from the kettle to storage tanks and then back to a succeeding kettle for the saponification change. These partly spent lyes may cool off on storage and in that condition the reaction between their caustic soda content and the fat charge is slow and uncertain.

TABLE XVII-2

(1) Saponification change
(2) Strong change   ⎫ Lyes to storage for use
(3) Strong change   ⎬ in saponification change
(4) Strong change   ⎭ in succeeding kettle.
(5) Fitting change

Countercurrent System. The third system of washes is the countercurrent system (see Fig. XVII-2). . . . In this system, a wash is pumped directly from one kettle to a succeeding kettle which is in an earlier stage of the process. The same wash will pass through a number of kettles until its countercycle is completed and it is transferred to the glycerine department as spent lye.

In larger soap plants, where the countercurrent system is used, kettles receive ten or more washes on a twenty-four hour a day kettle schedule with short settles between washes. The recovery of glycerine from the saponification of the fats is approximately 95% of that theoretically available. This recovery is accomplished with a ratio of less than 1 lb. of spent lye produced per pound of fresh fat or oil charged to the kettles.

In the medium or small soap plant, where it is not feasible to conduct a twenty-four hour a day schedule on the soap kettles, the countercurrent system is applicable, using about three large washes per kettle and overnight settles between washes.

(B) TYPICAL OPERATION OF THREE-WASH COUNTERCURRENT SYSTEM ON A FOUR-KETTLE UNIT

Proper operation of the three-wash countercurrent system requires units of four kettles of equal capacity. Each unit is independent of other units and handles one grade of soapstock in its four kettles.

The changes in each unit are so staggered that washes from kettles in a more advanced stage are pumped directly to kettles in a less advanced stage. For a three-wash schedule, the cycle of each kettle from the initial charge until the kettle is ready to be charged again is eight days. One kettle of the unit is finished every second day, thus

providing a steady, continuous supply of neat soap. A unit of four kettles will produce at the rate of approximately 3.5 lbs. of neat soap per day per cubic foot of kettle space.

Each kettle is charged with a weight of fresh fat equal to approximately three-tenths the gross capacity of the kettle calculated as water.

When the operation is started for the first time on empty kettles, the fat charge is increased above the normal charge by about 15% to allow for soapstock equivalent to that in a normal niger. The kettles are not put into operation simultaneously, but one is started on every second day until all are in operation. Washes are made up of fresh caustic lye, salt, and water, until washes from other kettles in the unit become available.

Fig. XVII-3 shows the schedule for the four-kettle unit in which the three-wash countercurrent system is used. The pattern of the eight-day cycle as shown is repeated continuously during the operation of the plant.

For the purpose of illustration, the flow sheet in Fig. XVII-3 is based on a kettle charge of 50,000 lbs. of fats and oils which yield, on saponification with caustic soda, 51,000 lbs. of anhydrous soap and 5000 lbs of glycerine.

If the kettle charge is greater or less than 50,000 lbs., the kettle compositions shown below will vary in proportion to the charge.

The composition (in pounds) of the kettles on each change is approximately as follows:

First Change

Curd

Anhydrous soap	46,400
Unsaponified fat	5,000
NaCl and other dissolved solids	900
Glycerol	2,360
Water	25,240
Total	*79,900*

Lye

NaCl and other dissolved solids	6,200
Glycerol	4,730
Water	50,470
Total	*61,400*

Second Change

Curd

Anhydrous soap	51,500
NaCl, NaOH, and other dissolved solids	1,000
Glycerol	1,055
Water	29,445
Total	*83,000*

Lye

NaCl, NaOH, and other dissolved solids	8,300
Glycerol	2,590
Water	72,310
Total	*83,200*

Third Change

Curd

Anhydrous soap	60,600
NaCl, NaOH, and other dissolved solids	1,200

Glycerol	405
Water	35,495
Total	*97,700*

Lye

NaCl, NaOH, and other dissolved solids	7,700
Glycerol	785
Water	68,715
Total	*77,200*

Fourth Change

Neat

Anhydrous soap	51,500
NaCl, NaOH, and other dissolved solids	300
Glycerol	270
Water	26,830
Total	*78,900*

Niger

Anhydrous soap	9,100
NaCl, NaOH, and other dissolved solids	900
Glycerol	130
Water	12,970
Total	*23,100*

Changes for kettle A only are described below. The same changes on the other kettles are performed in the same manner.

First Change. Change No. 1, sometimes called the *saponification* or *killing* change, is given to kettle A. The niger from the previous boil in this kettle has been pumped over to storage and the new boil is begun on an empty kettle. Vigorous boiling is carried out with open steam while the fatstock and the soap lye from Change No. 2 of kettle D are pumped into the kettle. The caustic strength of the lye is "spent" or used up in saponifying the fat charge. Additional fresh caustic lye is needed to carry the saponification further. Virtually complete saponification can be accomplished at this stage by skillfull operation and with sufficient time. However, it is practical to saponify only 85–90% of the fresh charge because the extra time required for complete saponification is not justified by any appreciable added benefit [and it is highly desirable at this point to have an excess of fat in the pan to be sure that the alkali in the lye is reduced to the very minimum—Au. Note].

It is important that a proper balance of electrolyte be maintained in the kettle during the saponification. . . . It is well to keep the soap in a semipasty or closed condition throughout this operation.

If saponification is carried out properly, it should take no more than two to three hours to saponify upward of 50,000 lbs. of fat to the extent of 90% of the fat charge.

Toward the end of the saponification phase of the first change the kettle begins to take up additions of fresh caustic lye more and more slowly. This is an indication that saponification has gone as far is practical. Before proceeding to grain-out the soap with salt, the kettle should be boiled thoroughly until there is no free caustic left. . . .

When the kettle is neutral, it is grained-out with dry salt. Concentrated brine is sometimes used but it increases the amount of spent lye unduly. Great care must be exercised in obtaining the right concentration of salt in the lye. Insufficient salt results in a spent lye containing a large amount of dissolved soap. Not only is this soap wasted

during the treatment of spent lyes, but its presence makes satisfactory treatment [expensive and] difficult.

Too high a salt concentration in the lye causes a condition known as *oversalting*. The curd has a *hard grain* and tends to hold a greater percentage of water than is normal. This reduces the efficiency of the glycerine recovery, since a greater portion of glycerine is retained in the curd and a lesser portion of glycerine is removed with the spent lye. [The excess salt is also likely to settle out on the bottom of the pan and to hinder closing operations on the subsequent boil—Au. Note.]

There are several methods of determining when a "grained" state has been completed. A sample of boiling soap is withdrawn from the kettle with a trowel. If the soap is in a grained condition, several drops of clear lye will separate from the curdy mass. If no lye separates from the mass, the kettle is still in a closed state and requires more salt. If the clear separated lye is dropped on a cold surface of metal or glass and, on cooling, remains clear, it is an indication that graining is complete. If, however, the drop of lye becomes opaque and milky, then additional salt must be added to complete graining-out.

A second method of determining if graining-out has been completed is to filter a small sample of clear lye from a mass of curdy soap taken from the kettle. Salt or concentrated brine is stirred into the clear lye. If further curds of soap separate from the clear lye, then graining-out is incomplete and more salt is needed for the kettle. If the lye remains clear, graining-out is complete.

Oversalting can be corrected by dilution of the kettle with water. However, it is best to avoid oversalting by approaching the end point of the graining operation with care.

A definite change in the physical appearance of the boiling soap can be detected when the end point is approached. When the kettle is properly grained, it is allowed to settle overnight.

Second Change. The spent lye which has settled out overnight from the first change in kettle A is discharged to the glycerine department for glycerine recovery. Kettle A is then given its second change. Enough water is added to the curd to just "close" the soap. At the same time, open steam is turned on in the kettle for agitation. When the soap has smoothed out to a pasty, closed condition, fresh caustic soda is run into the boiling kettle to complete the saponification of the change. Care must be taken not to add the caustic much faster than it will react with the unsaponified fat. An excessive concentration of free caustic will grain-out the soap and retard saponification. Complete saponification can be achieved in a relatively short period of boiling in the closed state with but a slight excess of caustic.

When the charge is completely saponified and no longer reacts with a slight excess of caustic in the kettle, soap lye is pumped over from the third change of kettle D. While this lye is being added, constant agitation with open steam is maintained. The kettle is then grained-out with fresh caustic or [preferably] dry salt [or brine] and allowed to settle overnight.

Third Change. The soap lye which has settled out overnight from the second change in kettle A is pumped over to kettle B, which is being given its first change.

Change No. 3 is then given to kettle A. As in change No. 2, the curd is closed up with water while being agitated with steam. To make doubly sure of complete saponification, a small addition of fresh caustic is run into the kettle and boiling is continued for a short period while the kettle is in a closed state.

Niger is pumped from storage into kettle A with constant boiling. The wash is built up to the desired size and the kettle is grained-out with brine or caustic or a combination of the two.

It is to be noted that the relative concentration of NaCl and NaOH on this change will be the same as found in the neat soap after the kettle is fitted and settled. Hence, regulation of the relative NaOH and NaCl content of this change affords a means of adjusting free NaOH or NaCl in the finished neat soap.

When the wash has been built up to proper size and the kettle is grained-out, it is allowed to settle overnight.

Fourth Change. The lye from the third change of kettle A is pumped over to kettle B for the second change of the latter.

Change No. 4, the *fit,* is then given to kettle A. This is a critical operation and requires considerable experience in its accomplishment, since it is difficult to determine beforehand by analytical means the correct amount of water to be added. After the soap lye has been pumped from kettle A to kettle B, the curd is boiled on open steam and the proper quantity of water is added gradually to the kettle to obtain the type of fit desired. Webb[4a] describes the fitting operation in detail, especially in regard to the types of fit from *coarse* to *fine.* Roughly 4 or 5 lbs. of water, including steam condensate from the open steam coil, is required for every 100 lbs. of normal curd soap to obtain a "medium" fit.

If too little water is added on this change, an extremely coarse fit is obtained which settles out little dirt and produces neat soap which is short in character and unsuitable for further processing.

On the other hand, an excess of water produces a viscous, waxy mass which will settle out a niger only with difficulty. The soap handles poorly, if at all, on further processing.

The trowel test as described by Webb[4a] is the best practical guide for the correctness of the operation. This is an empirical test depending on the degree of tackiness possessed by the kettle soap. Tackiness is measured by observing how hot soap dipped up from the boiling kettle slides from a tilted trowel.

A definite correlation can be noted between the way the soap slides off the trowel and the type of fit. In coarsely fitted kettles, the thin layer of soap has a tendency to break up into flakes as it leaves the trowel and the surface of the trowel dries off almost immediately. In finely fitted kettles, the soap is tackier and tends to drop off the trowel without flaking, leaving the surface of the trowel greasy to the touch. In intermediate fits, the soap has less tendency to flake than in coarse fits and the surface of the trowel requires a few seconds longer to dry after the layer of soap has slipped off.

With experience, a soapmaker can observe the progress of the fit by the appearance of the boiling mass of soap.

Wigner[3] describes in detail a method of conducting the fit by adding a predetermined amount of water calculated from the proportion of electrolyte, anhydrous soap, and water present in the curd. This method appears to have good possibilities for quantitative control purposes when properly standardized.

If, by chance, an excessive amount of water has been added on the fit and the soap is too thick, this condition can be corrected by the addition of a small amount of salt or caustic. However, it is best to avoid such a condition, since the addition of extra salt or caustic during the fit will produce excessively large nigers.

When the proper degree of fit has been obtained on kettle A, it is allowed to settle into the two layers, neat soap and niger. The period of settling will vary according to size of kettles, type of fit, and soap base. Large kettles take longer to settle than small ones. Fine fits require a longer settling time than coarse fits. Kettles containing rosin

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[4a] E. T. Webb, *Soap and Glycerine Manufacture,* Davis, London, 1927.

in the soap base require a longer settling period than straight tallow or grease-base kettles.

After proper settling, the neat soap layer is pumped to storage or directly to processing. When the neat soap has been entirely withdrawn, the niger is boiled up with open steam, and is pumped to niger storage for reuse in a succeeding kettle.

If the niger is excessively dark, it may be cleaned up by an operation called a *pitch*. This is done by diluting the niger with a small amount of water while boiling it with open steam and then allowing it to settle. A dark sludge will settle to the bottom of the kettle. This mass is discarded, or, if it contains enough soap, it may be used as a soap-stock for a low-grade soap. The balance of the niger is pumped to niger storage for reuse.

(C) Three-Kettle Unit Operation

In the first change, saponification is carried out with fresh caustic, but is not pushed farther than about 95% of the fat in the charge and the lye must not contain more than the minimum allowable from the point of view

TABLE XVII-3

Three-Kettle Countercurrent Wash Plan[2]

Day	Kettle A	Kettle B	Kettle C
1	Change No. 1. Lye to glycerine department	—	Change No. 3. Lye to *A*
2	Change No. 2. Lye to *B*	—	Settle
3	Change No. 3. Lye to *B*	Change No. 1. Lye to glycerine department	—
4	Settle	Change No. 2. Lye to *C*	—
5	Neat pumped	Change No. 3. Lye to *C*	Change No. 1. Lye to glycerine department
6	—	Settle	Change No. 2. Lye to *A*
7	Change No. 1. Lye to glycerine department	—	Change No. 3. Lye to *A*

of the standard of *the maximum allowable per cent alkali in the spent lye*. Consequently, this lye can be sent straight into the glycerine department. Since this lye is also the result of the first saponification, it is likewise sufficiently concentrated with regard to glycerine. The size of the wash may be regulated to an amount which will remove 70% or residual free glycerine[2] from the kettle as follows. Let us assume that we succeed in obtaining a quite "efficient" curd with only 35% entangled (occluded) lye. In this case, the curd will contain 65% soap and, correspondingly, 60% fatty acids. 70% of glycerine removal means that:

$$\frac{100x}{x+35} = 70, \text{ hence } x = 81.5$$

the weight of curd being taken as 100 and the weight of the separated lye as x.

In absolute figures, conditions must be regulated as to have in the pan a total weight of 181.5 kg. of soap mass to every 60 kg. of fatty acids, from

which 81.5 kg. of lye should be separated. This can be expressed in other terms, namely, that a 70% glycerine recovery can be ensured in one wash when the proportion between the weight of the fatty acids to that of the lye separated amounts to 1 : 1.36.

"In the second change, saponification is completed by *closing* the curd with water and boiling it in that state, with an excess of fresh caustic, for an hour. This wash is also built up to remove 70% of the residual free glycerine."[2] This lye must be turned over to the second kettle in a countercurrent system for two reasons: first, because it contains more alkali than allowed by the standard; second, because it is too low in glycerine.

"In the third change, this wash, unlike the first two washes, is built up entirely of fresh brine or caustic and added water. The removal of residual glycerine from this change is 50%."[2]

$$\frac{100x}{35+x} = 50$$

This time, to 60 kg. of fatty acid in the kettle there is 135 kg. of total weight, and out of this only 35 kg. of lye separate. Consequently, the ratio this time between fatty acid and lye is 1 : 0.7.

"In the settle, the niger retains about one-third of the small amount of glycerine left at this stage."[2]

The following are the performance standards which can be accomplished when operating under the above flow plan, with a charge of tallow yielding 10% of its weight in glycerol:

(1) Net kettle recovery of glycerine: 94% of theoretical.[2]

(2) Ratio of pounds of spent lye to pounds of net kettle fat: 1.35/1.00.[2]

(3) Concentration of glycerine in spent lye: 7% by weight.[2]

(4) Production capacity per six-day kettle cycle: 24.5 lbs. neat soap per cubic foot kettle space.[2]

(5) Ratio of glycerine recovery in the three washes: 70/70/50.

(D) GLYCERINE RECOVERY AND THE KETTLE PLAN

It is obvious that, when the ratio of glycerine recovery in the washes becomes smaller, for instance, 60/60/40, the total percentage of glycerine recovery also becomes smaller, but at the same time the concentration of the spent lye in glycerine becomes higher. The 60/60/40 ratio means smaller lye-bulk, or, in other words, a smaller proportion of lye to a certain weight of fatty acid or fatstock in the kettle and vice versa. As stated when dealing with the production standards, the soapmaker must make up his mind whether in each case an additional glycerine recovery would still be a paying proposition. Fig. XVII-3[3] illustrates the point very well.

A formula has also been advanced by Govan which makes it possible to calculate the highest practicable yield of glycerine when it has been decided which system of washes should be used under the countercurrent system.

In his lecture, Govan[4] adds to his explanation of 1942 the following consideration:

Fig. XVII-3 (see also Fig. VI-4) shows a comparison of pounds of spent lye produced per pound of fat charge at varying levels of glycerine recovery for both the individual and the countercurrent wash systems. Each system employs three washes.

Glycerine recovery from the kettles for the individual wash system is derived from the formula:

$$\% \text{ Glycerine Recovery} = \frac{300\,(L + M + N - LM - LN - MN + LMN)}{2 + L + M + N - LM - LN - MN + LMN}$$

L, M, and N represent the fractions of free glycerine in the kettles removed in each of the three changes.
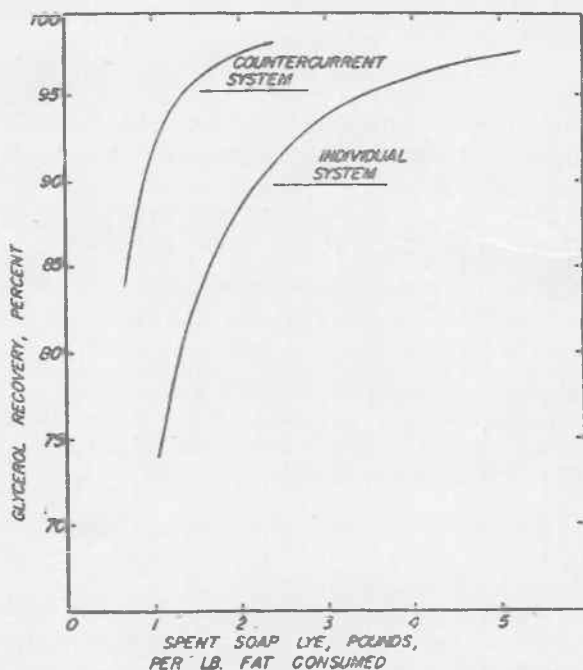
Fig. XVII-3. Glycerine recovery in the individual and the countercurrent wash system.[4] Abscissa, spent soap lye in pounds per pound of fat consumed. Ordinate, per cent glycerol recovery.

In like manner, glycerine recovery for the countercurrent system is derived from the formula:

$$\% \text{ Glycerine Recovery} = \frac{200L\,(0.9 - 0.9N + 1.4MN + 0.1M)}{2 - 2N + 2MN - 2M + 2LM + LMN}$$

The letters L, M, and N represent the fraction of free glycerine removed on the 1st, 2nd, and 3rd changes respectively.

Saponification in the countercurrent system is taken to be 90% complete in the first change and 100% complete in the second change. For simplicity, saponification in the individual wash system is taken to be complete in the first change.

In both systems, the composition of the curd is assumed to be 62% anhydrous soap and dissolved solids and 38% aqueous. The lye layer is taken to consist of 10% dissolved solids and 90% aqueous. On the settle, the distribution of glycerine between the neat soap layer and the niger is taken to be in the ratio two to one.

The ratio of spent lye to fat charge for each definite glycerine recovery is calculated using the above compositions for curd and soap lye.

For illustration, the values for L, M, and N used for the countercurrent flowsheet in Fig. XVII-2 are 0.67, 0.71, and 0.66, respectively. On substituting these values in the above formula for countercurrent glycerine recovery, the percentage of glycerine recovery from the kettles is found to be 94.7%. The ratio of spent soap lye to fat charge is 61,400 lbs. lye to 50,000 lbs. fat, or 1.23 lbs. of lye to 1 lb.

It may be pointed out for greater clarity that the fractions L, M, and N are determined from the composition of the curd and the soap lye. With reference to the flowsheet in Fig. XVII-2, the amount of water plus glycerine on the first change is 27,600 lbs. in the curd and 55,200 lbs. in the lye. The total water plus glycerine in the kettle is therefore 82,800 lbs. The amount in the lye, 55,200 lbs., is the fraction 0.67 of the total amount of water plus glycerine in the kettle. Therefore, fraction L equals 0.67 in the first change. Fractions M and N are derived in the same manner for the other changes.

Other points in the curves are derived in the same manner as in the above illustration. However, it must be noted that in the individual wash system the total amount of spent soap lye produced per kettle is found by adding together the three washes.

An inspection of Fig. XVII-3 indicates that a 95% kettle recovery of glycerine is practicable for the full countercurrent system of washes, whereas only 85–90% appears to be the practical limit for the individual wash system.

Even at the level of 85–90% recovery in the individual wash system, costs of treating and evaporating the spent lye produced are considerably more than for a 95% kettle recovery in the full countercurrent system.

Therefore, it appears that it is advantageous to use, wherever possible, the full countercurrent wash system instead of the individual wash system. . . .

It is felt that the derivation of the equation used for estimating glycerine recovery in the full countercurrent system will be of value. This is given below:

Let L = fraction of free glycerine in kettle removed by first wash.

M = fraction of free glycerine in kettle removed by second wash.

N = fraction of free glycerine in kettle removed by third wash.

a = glycerol in niger.

s = glycerol bound in unsaponified portion of fat charge in first change.

y = glycerol in the lye from a second change.

z = glycerol in the lye from a third change.

R = fraction recovered of available glycerol in the fat charge.

l = available glycerine in the fat charge.

Then

$$R = L(l - s + y) \tag{1}$$
$$y = M(l - L)(l - s + y) + s + z \tag{2}$$
$$z = N(l - M)(l - L)(l - s + y) + s + z + a \tag{3}$$

Solving (2) and (3) simultaneously, the following value for y is obtained:

$$R = L \left(l - s + \frac{M(l - L + Ls + Na)}{l - N + MN - M + LM} \right) \quad y = \frac{M(l - L + Ls + Na)}{l - N + MN - M + LM} \tag{4}$$

Solving (4) and (1) simultaneously, the following value for R is obtained:

$$R = L \left(l - s + \frac{M(l - L + Ls + Na)}{l - N + MN - M + LM} \right) \tag{5}$$

Now if it is assumed that the charge of fat is 90% saponified on the first change, then the fraction s representing the glycerol bound in in the unsaponified fat is 0.1, and (5) becomes:

$$R = L \left(0.9 + \frac{M(l - 0.9L + Na)}{l - N + MN - M + LM} \right) \tag{6}$$

Now if it is assumed that on the fitting change the free glycerine is divided between the niger soap and the neat soap layers in the ratio of one to two, respectively, then since the glycerine in the niger is represented by a, the glycerine in the neat soap can be represented by $2a$. It then follows that:

$$R = l - 2a \quad \text{or} \quad a = (l - R)/2 \tag{7}$$

where R is the fraction recovered of the available glycerol, $2a$ is the glycerine lost in the neat soap, and l is the available glycerine in the fat charge. Solving (6) and (7) simultaneously, the following value for R is obtained:

$$R = 2l \frac{0.9 - 0.9N + 1.4MN + 0.1M}{2 - 2N + 2MN - 2M + 2LM + LMN} \tag{8}$$

Multiplying both sides of the equation by 100:

$$\% \text{ Recovery} = 200L \frac{0.9 - 0.9N + 1.4MN + 0.1M}{2 - 2N + 2MN - 2M + 2LM + LMN} \tag{9}$$

which is the recovery formula for the full countercurrent wash system.

(E) Use of an Auxiliary Kettle

Another kettle plan should be discussed at this point to demonstrate how local circumstances may alter the way in which production is carried out.

In a soap factory where mainly household soap containing 50% coconut oil and 50% peanut oil is produced and where the main consideration is kettle output rather than maximum glycerine recovery, quite a different kettle plan has been adopted.

There were 4 large kettles with about 110 cubic meters total kettle space and 2 smaller kettles with 30 cubic meters additional space. Peanut oil for the fat charge originated from different sources: soapstocks, foots recovered from spent bleaching clay, and other soapery foots and purified peanut oil. The practice was to treat the dark soapstocks and foots in the smaller kettle by saponification, and by several brine washes when necessary. In this case, only the first lye was sent into the glycerine department, care being taken that no large excess of alkali was left in them. In the meantime, the niger left in the large pans with its excess alkali was neutralized by boiling with

some peanut oil. On the same day, some of the peanut soap produced from soapstock or foots was pumped over into the large kettle, strengthened by boiling with some additional lye, and grained with salt. The next day the coconut oil was pumped into the curd in the large pans, saponified, and fitted.

In this way, good neat soap in a suitable proportion of fat in neat to niger (2/3 to 1/3) was withdrawn from the large kettles every second or third day. In a kettle space of 140 cubic meters, 383 tons of best quality household soap were produced during one month. These figures, calculated on a six-day or one working week kettle cycle, allow for the production of 680 kg. per cubic meter of kettle space. In comparison to the countercurrent kettle plan which yielded a production capacity of 390 kg. per cubic meter only, the second plan ensures a much higher performance. However, it must be borne in mind when drawing conclusions that the second plan yields a very poor glycerine recovery. Such a plan should be adopted only when production is rather forced, where sufficient kettle space is not available, and finally, where glycerine recovery, for some reason or another, is not very important or is not a paying proposition. It must also be stressed that the household soap produced by the second kettle plan always contained up to 1.5% glycerine and that a high glycerine content in soap is known to be undesirable in certain circumstances.

(F) THE RUSSIAN KETTLE STANDARDS

It is of interest to note the developments which occurred in the soap industry of Russia during the years just preceding World War II when that country had to produce soap for a very large population without sufficient equipment. The soap industry, like others in Russia, is organized on a national basis and production plans are formulated and executed accordingly.

At a national conference of the soap industry, production and kettle plans were discussed and a minimum performance standard was adopted and made obligatory. These performance capacities were worked out for four different sizes of soap kettles, ranging between 60 and 200 cubic meters. The Russian standards specified for these four sizes of kettles and for the various operational details are reproduced in Table XVII-4.[5a]

Very great efforts were made by Russian soap technologists in the following years with the object of increasing the efficiency of their equipment even further. A summary of these efforts appeared in Tosseiyev's *General Course of Fat Technology*.[5b]

The need for a lengthy settling of the soap mass when obtaining the neat layer above the niger, the fact that the latter comprises only one-fourth of the

[5a] F. Kasatkin, *Masloboine Zhirovoe Delo* (1936), 355.

[5b] G. S. Tosseiyev, *General Course of Fat Technology*, Moscow, 1940, p. 518.

entire capacity of the pan, and the fact that only 85% of the total fat charge
goes into the neat soap—all greatly decreases the output of the pan—the out-
put of neat soap per cubic meter per 24 hours.   Actually, until recently, in
Russia, this output was only 0.17–0.20 ton.   In European countries, because

TABLE XVII-4
RUSSIAN KETTLE STANDARDS[5a]

	Allowance in hours, for curd soap				
Category	Saponifi-cation	Analysis and adjustment	Removal of soap	Loss of time for cleaning, repairs, and transition	Total allowance
I	6	5	1.5	0.5	13
II	7	5.5	2.5	1	16
III	8	6	4	1	19
IV	10	6.5	5	1.5	23

	Allowance in hours, for neat soap							
Category	Saponi-fication	Salting-out	Fitting	Settling	Removal	Salting-out on niger	Loss of time for repairs, etc.	Total allowance
I	6	4.5	2.5	24	1.5	3.5	2	44
II	7	5	3	26	2.5	3.5	3	50
III	8	5.5	3.5	28	4	4	3	56
IV	10	6	4	30	5	4	3	62

Category I .... up to 60 cu. meters
        II .... 61–100 cu. meters
        III .... 101–150 cu. meters
        IV .... 151–200 cu. meters

The following yields, in tons per 1 cu. meter kettle capacity per 24 hours, were ac-
cordingly established:

Category	Curd	Neat
I	1.477	0.273
II	1.28	0.24
III	1.01	0.214
IV	0.83	0.194

These standards were calculated for carbonate saponification of 75% of all free
fatty acids, rosin, etc. of the fat charge. Output of ready soap taken as 80% of kettle
capacity for curd, 50% for neat (for square kettle the curd output has been fixed at
75%).

of the use of coconut oil in the fat charges, and the necessity to allow longer
settling times, the output per pan is lower than the figures mentioned above.
    At the production conference of 1936 in Russia somewhat higher stand-
ards of net neat output were established—0.19–0.27 ton per cubic meter (de-
pending on the capacity of the pan).   This should have been achieved

through increased filling of the pans in the saponification process, and a decrease in settling time. Although these standards are a step forward, they still constitute an inadequate exploitation of the output possibilities of the pan.

Just before the war some Russian factories have achieved a considerable increase in pan output through a rational utilization of its capacity and through a change in the condition of boiling. When the soap mass is settled in the pan after partial salting, the main part of the niger settles rather quickly, in 1–3 hours, while the settling of the rest of the niger takes a longer time. Therefore, Chalevsky[5b] proposed removing the part of the niger already settled from the pan after the partial salting, without waiting for complete settling. The vacated capacity of the pan is refilled with soapstock and also with neat obtained through salting-out and fitting (in an auxiliary pan) of soapstock, raw soap, niger from previous boiling, etc. Later, the soap is fitted and settled for a short period, as the dirtiest niger has already been removed. In this way, the output of the pan is increased through its supplementary charging, which takes the place of the removed niger. Besides, it is increased through the parallel treatment of the niger, soapstock, etc. in the auxiliary pan, while previously this was done in the main pan. All this helps toward a considerable increase of output up to 40% or more.

As a further development, Moisseyev[5b] proposed, instead of salting down to spent lye as in the indirect boiling method, salting in such a concentration as to bring about separation into three phases—neat, lye, and niger. After two to three hours settling, the spent lye and the main mass of the niger are removed to the auxiliary pan where soapstocks are treated. Their neutral fat combines with the free alkali of the spent lye and the niger. The liberated capacity of the pan is refilled with offal and neat obtained in the auxiliary pan from soapstock, rosin soap, and niger, after which fitting is carried out, which usually requires a short settling period of about 15 hours.

A further increase in pan output, according to a proposal of Bogod,[5b] is achieved through increasing the concentration of the unsettled soap before fitting. Usually, such unsettled soap contains not more than 50–52% fatty acids, as a high concentration makes it too viscous and renders final operations difficult. It is possible, however, to overcome this by choice of concentration of electrolyte in the soap mass. For the usual fat charges used, this decrease in viscosity is achieved at a total $NaOH + NaCl$ of 0.9% instead of the usual 1.2–1.4%. The Na_2CO_3 content is 0.4–0.7%. Thus, the fatty acid content of the unsettled soap, before fitting, is raised to 55–56% and higher without increasing its viscosity. After settling of the soap fitted under these conditions, the content of niger and its fatty acid content are decreased, together with the duration of settling (12–15 hours). All this brings about a

considerable increase in output (100% and more) as compared with the 1936 conference standard.

The following kettle performances are claimed by the various Russian authors for their respective boiling systems.

Chalevsky: 350 kg. of neat soap per cubic meter of pan capacity in 24 hours in vats of 60–100 cubic meter size.

Moisseyev: 338 kg. in 24 hours in a 100 cubic meter pan per cubic meter, or 450 kg. in 24 hours in the main pan when not counting the auxiliary kettle.

Bogod: 770 kg. per cubic meter in 24 hours.

SETTLED SOAPS

(1) Curd Soaps Settled on Clear Lye

Settled soap may also be called curd soap boiled on clear lye, owing to the method of finishing applied. Such soaps were manufactured in the past, before the introduction in the industry of such raw materials as coconut oil or the other fats containing low molecular fatty acids. Finishing by partial salting-out is only a comparatively recent development, while, in the past, it was regarded as quite satisfactory to have the finishing of the soap done by complete salting-out and the product settled finally on the clear lye. In fact, it would yield quite an oversalted curd if the same thing were tried with a fat mixture containing a high proportion of coconut oil. On the other hand, it is known that it is not a simple matter to fit the soap of an oil having a very low F.L.C., and it will be recalled that Merklen, in his classical experiments, reported that he was unable to achieve proper fitting with certain soaps, just as he had difficulties in salting-out completely the soaps of coconut oil.

There is another reason why, in certain cases, the soapmaker prefers to finish his soap "curd" on clear lye instead of by the process of fitting. Low titer fats or oils generally yield soft soaps when finished by fitting and it was found that the same soaps become much harder when boiled on strong salt lyes. It is also possible, by this practice, to produce a curd soap containing a higher percentage of fatty acids than was thought possible when using the ordinary finishing procedure normally applied in the full-boiled process. The higher fatty acid content may be responsible for the hardness of such soaps boiled on strong salt lyes. In view of the discovery of kettle wax areas in the phase diagram by McBain and co-workers, we tend to suppose that this kind of hard soap probably consists of soaps belonging to one of the kettle wax "islands," such soaps consequently being neither neat nor curd soaps.

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Wigner[6] reports that in one instance an attempt was made by him to boil peanut soap on salt solutions of gradually increased concentrations. This was done in the hope of obtaining a harder soap than generally produced when peanut oil is saponified and grained. No marked effect was obtained, however, until the strength of the salt solution approached 17%, but continued boiling on this lye produced a soap of satisfactory hardness. It will be remembered that Wigner's 66% rule implies that for a certain set of salt concentrations in the lye and in the corresponding curd there is only one fixed fatty acid concentration possible in the curd. In this mixture of the hard peanut oil soap boiled on 17% salt solution, the corresponding values, however, did not fit in the 66% rule and as an explanation for this phenomenon Wigner erroneously suggested that this particular soap contains a pure soap hydrate with 70% instead of 66% fatty acids. This could be understood as stating, in other terms, that this particular soap belongs to an altogether different soap phase and that this would account for its different properties.

(A) TYPICAL FAT CHARGES FOR MAKING CURD SOAP

Tallow-palm oil 50:50. Red oil-tallow-rosin 50:20:30. Tallow. Palm oil. Olive oil.

(B) THE PROCESS

(a) *"Killing" Change—Saponification.* With curd soap, the pan is always empty and it is the fats which are charged into it first and melted with direct steam. When only fat is in the kettle and boiling is conducted over an open fire, it is necessary to start saponification with diluted lyes. Nowadays, however, when steam is blown first into the fat charge, there is always enough condensed water in the kettle to dilute the strong lye on entering. It is difficult to state for each case the exact strength of the caustic lye required at the beginning. It depends very much on the nature of the fats used in the charge. It has been pointed out on several occasions that the L.L.C. of the different fats varies considerably, and it is this concentration which should never be exceeded in the kettle, at any moment, in order to keep the mass in a "closed" state. For this reason also, the lye should not be charged in a continuous stream, but should rather flow over some kind of distributor which sprays the lye all over the pan surface in uniform droplets.

The caustic solution is generally stored at a concentration of 38° Bé and can safely be used as such, even at the beginning, provided that, at the very start, the fat charge had been thoroughly boiled through with open steam, with sufficient condensed water formed, and provided further that the lye is charged in small portions and well distributed as described. There is also less danger of losing the closed appearance of the boil if the charge contains

[6] J. H. Wigner, *l.c.*, p. 40.

considerable amounts of free fatty acids and, in the latter case, the addition of strong caustic can go on at a quicker pace than when only neutral oils are present. Nevertheless, in most soaperies, the first batch of alkali run into the kettle is kept at a strength of 15° Bé even when open steam boiling is practiced.

We have dealt, on several occasions, with the conditions which must be controlled in order to obtain a well ordered saponification process (see Chap. II, 6). It will be remembered that the initially formed soap is known to act as an emulsifier provided that sufficient water is present as a guarantee against separation into the components. The soap acts as a catalyst, the saponification reaction taking place within or on the surface of the soap micelles. Electrolyte-free soap solutions tend to be rather viscous, and it is for this reason that the pan contents, at any moment of the boil, must be provided with a certain minimum amount of nonreacting electrolytes. Caustic would act as a conditioner for easy boiling for a certain restricted period only, because it would gradually be spent, leaving the pan contents without electrolytes, so that the mass would again become viscous and heavy-boiling. It is for this reason that some soapmakers choose to "reduce" their caustic lyes by adding a certain amount of soda ash. The addition should not exceed 5%, since more than this would probably upset the normal course of the process. It has been stated by certain soapmakers that curd soaps turn out to be of a better consistency when "reduced" caustic lyes containing soda ash had been used. It is, of course, obvious that the addition of a salt solution in cases of emergency would also help to thin out the boiling mass, but there seems to be truth in the statement that salt-reduced lyes produce somewhat more brittle soaps.

A further portion of caustic should only be added when the former portion had already been absorbed by the boiling mass and the mass remains in a well "closed" state. We can distinguish this state from the other, undesirable, open condition by taking out a sample of the soap on a well-warmed wooden paddle and observing that the mass runs down in form of a homogeneous plate, but not in drops or curdled granules.

Excessive heat should not be employed, for this would obviously not be a good condition for the forming of an emulsion. The open steam, at the beginning, is, in fact, used less for heating than for agitating purposes. It is therefore difficult to say how strongly the mass should be boiled at the beginning. Low temperature aids emulsification.

Once emulsification has set in, the boiling mass becomes of milky white appearance, which gradually gives way to a darker translucent aspect, with saponification progressing steadily. Approaching the end of the saponification process, we enter the danger zone of bunching (see Chapter XVII). Bunching occurs when no caustic or electrolytes remain in the almost totally

saponified fat. At the slightest sign that bunching has set in, one should not hesitate to add at once some more caustic or any other electrolytes at hand. It is always easier to dispose of the excess chemicals in the soap than to correct a mass of bunched soap. As a preventive measure against bunching or, more generally, against excessive viscosity of the soap mass, it is advisable to add to the mass at this stage some 2° Bé salt solution. It should be pointed out that it would be a great mistake to attempt to prevent or even to disperse thick or bunched soap by mixing water into it, since the phase diagrams indicate clearly that in such cases the formation of middle soap will occur.

The necessity of employing quantitative methods should again be emphasized. The soapmaker will know from his records the exact quantity of saponifiable fats he is to treat and also the amount and strength of caustic soda he is going to employ for saponification. It has been good practice to run in the caustic solution from a tank in which provision for exact measurement of the quantities is made.

A manometric gage attached to the kettle also greatly aids the attendant in judging the exact amounts of materials involved at any moment in the process.

With an eye on the indicator of the caustic container tank, the operator can see at a glance when the process of saponification is approaching its conclusion. No matter how exactly the calculation and weighing of fats and lyes were performed, it is impossible to conclude the saponification by adding the exactly calculated amount of caustic to the fat. The smallest differences in the determination of the saponification value of the fat charge, or a minute variation in the measured strength of caustic lye, will upset the calculation. Consequently, when the measured amount of caustic soda is run into the kettle, the soapmaker knows that the kettle contents must, at this stage, be very near the point of complete saponification. At this stage, the soapmaker carries out a few practical tests.

(a) A sample is taken from the pan on a well heated paddle and its consistency and appearance are examined. The sample should slide down the inclined paddle in a homogeneous, somewhat thick, gluey and transparent mass.

(b) A sample is taken from the paddle and is kneaded between thumb and forefinger. On cooling, the soap should be of a certain cohesive consistency and not a brittle, crumbling, or soft mass.

(c) A small quantity of soap should be clearly soluble in distilled water (no unsaponified fat present). Another test for unsaponified fat, when present, is the following: a small quantity of soap of the size of a shilling or a quarter dropped on a glass plate, on cooling, displays grey rings at the periphery.

(d) Tasted at the tip of the tongue, it should have a definite bite (free caustic present).

(e) Tested in alcoholic solution with phenophthalein, it should develop a pink color.

The bite test of the soapmaker is not an exact method for finding the real

alkalinity of the soap and is not a substitute for exact laboratory analysis as described later.

The use of thymolphthalein as suggested by Wigner gives a very distinct end point in the presence of Na_2CO_3. Lyes containing 0.01 to 0.02% caustic soda colors the indicator paper a faint blue, and 0.1% turns it into a definite blue color. Pale blue indicates the proper concentration of free caustic at the end of the saponification process.

Suppose the tests, as explained, do not show the presence of free alkali, then, of course, some alkali should be added at once and the boiling continued. If the repeated test now shows that at last some free alkali is present, the boiling should be continued until repeated tests prove that the alkaline reaction does not disappear. At this stage, the soap is also clearly soluble in distilled water. However, should the bite or the indicator reaction show that the soap contains too large an excess of caustic, then some fatty acid or neutral oil should be added and boiled until the excess alkali is again consumed. As an ideal condition, we must regard a state in which all fat is saponified and the mass containing not more than 0.1–0.3% NaOH.

The following are some practical tests for complete saponification and proper alkali content of the soap:

A drop of the soap of the size of a large coin deposited on a glass plate should remain clear and transparent for a short while, but gradually, on cooling, it should lose its transparency and become stuck to the plate.

No fluid should separate from the solid part during and after cooling; when such fluid separates, it is due to excess alkali and it is called, in the practical language of the soapmaker, a *lye ring*. Soap is more susceptible to excess electrolyte in the cold than when still in the hot state and it is for this reason that the lye separates after cooling, while no separation of the lye ring takes place in the hot soap sample. When a lye ring is observed, the soapmaker must make a correction by adding some fat to the kettle.

The test should also not show a grey ring (or fat ring) on cooling which indicates the presence of unsaponified fat.

The completely saponified and sufficiently alkaline soap should be a clean, homogeneous, and fairly viscous solution which should spin in long threads when running down from a hot wooden paddle, and also form threads between thumb and forefinger when tested before cooling completely.

By proper regulation of the process it is possible to saponify the fat charge in one change (see Chapter II for discussion of the necessity of a separate strengthening change). However, circumstances sometimes prevail, which cause the attendant to decide to apply one or more additional changes. This becomes necessary when dark fats are used or when thorough glycerine recovery is regarded as essential. In such cases, there is no disadvantage to leaving a small amount of unsaponified fat at the end of the first change, since this small quantity can then be easily saponified on the occasion of the second change.

For the saponification of the last traces of fat, it is advantageous to have the last portion of the caustic charged at a high concentration, preferably above 30° Bé (this, of course, depends again on the electrolyte susceptibility of the particular fat) into a fairly thick gluelike soap. This consistency should not be pushed too far, and it is an important rule that the soap mass must always retain its fluidity. Control is maintained by adding small quantities of water and brine. However, it must be borne in mind that too much water may cause an excessive increase in the lye bulk, resulting in increased cost of glycerine recovery.

In any case, utmost care should be taken not to add, at this stage, too much caustic, salt, or any other electrolytes, and it should be made a rule that for the final saponification the soap mass must remain absolutely "closed."

The practice of boiling the soap with strong alkalies in a separated state for long periods of time in order to saponify the last traces of fat has been abandoned in modern factories, as it does not accomplish its purpose. The "strengthening change" (see Chapter II) as formerly used can now be dispensed with, since boiling with steam has been introduced everywhere. It has been explained that boiling in the open state with excess alkali was only necessary in the past in kettles heated with direct fire in order to prevent the scorching of the soap on the directly heated surface. Soap in the open state is separated into soap hydrate and lye and it is always the water of the lye which is in direct touch with the kettle walls.

(*b*) *First Change—Graining.* The totally or partially saponified soap mass is now retested. When its appearance is normal and it possesses sufficient "fluidity," it is ready for salting-out. As has been explained, in order to obtain an efficient curd it is absolutely imperative to salt-out the curd on a lye whose concentration does not exceed considerably the L.L.C. of the particular formulated fat mixture. An "oversalted" curd not only contains too much salt, but is also low in fat and retains too much entangled lye. Such an inefficient curd has a negative influence on the process of glycerine recovery and will also cause the curd to retain too much electrolytes, yielding a hard, brittle or sharp soap.

After many years of experience, the soapmaker is able to judge by the appearance of the boil and of the soap sample on his paddle whether or not the graining is carried sufficiently far. It is convenient to use dry salt in order to avoid further dilution, but it is necessary to spray the dry salt in small batches on the surface and give the salt sufficient opportunity to dissolve and to disperse throughout the contents of the kettle. The quantity of salt to be added depends on: (*a*) the L.L.C. of the fat mixture; (*b*) the electrolyte content of the mass at the moment before graining is started; and (*c*) the water content or state of dilution of the pan. Brine has the advantage

of containing the salt in well-dissolved form, and there is no danger whatso-
ever of the dry salt upsetting the equilibrium at some isolated point of the
kettle space by escaping for a time the dissolving action of the water. Brine
lends itself also for easier measuring; it can be stored in a tank and the
quantities pumped or conveyed into the soap kettle can be measured at a
glance on the indicator.

Both brine and dry salt should be added while vigorous boiling is main-
tained in the kettle. It is only in the well-boiling kettle that the salt is able
to display its full graining action. It should be borne in mind that electro-
lytes show different degrees of graining action at different temperatures. Salt
should be added in batches and a sufficient period of boiling allowed before
a new batch is added. Under no circumstances should the whole amount of
salt be dumped into the kettle at one time.

As graining progresses, the heavy mass begins to boil in a less viscous
manner. When completed, the appearance of the surface changes completely.
The curd appears on the surface in a system of plates separated by furrows,
which constantly disappear in the mass and re-form again on the surface,
causing the "surface phenomenon" referred to by the soapmaker when he
remarks that "the soap boils in plates."

When the surface of the soap becomes rough and furrowed so that a
sample taken on the paddle shows it to be heterogeneous, and when the soap
stops sliding off the paddle in translucent and coherent sheets, it becomes
evident that separation has set in. From this moment onward, great care
must be taken to boil thoroughly before any new addition of salt or brine is
made and only small amounts of salt should be added, since otherwise the
risk is run of oversalting the boil. The proper appearance of the boiling
surface of the soap at the moment when it is sufficiently salted-out has been
compared to milk curd, but it seems that it can more adequately be described
as a white wool-like mass. When a sample is taken on a paddle, the soap curd
separates in fairly large white grains, from which clear lye separates and
trickles down when the paddle is held at a sloping angle. The operator
should make sure at this point that the appearance of the soap does not change
when boiling is continued. It could happen that the curding of the surface
was obtained as a result of the salt having been locally concentrated. In such
cases, continued boiling causes the dispersion of the local salt concentration,
and a deficiency of salt again becomes evident. It might well be that some-
where in the mass there exists undissolved or undispersed salt, but prolonged
boiling with open steam might lead to excessive water condensation and the
dilution of the pan contents would then necessitate the addition of a new
batch of salt.

Oversalting is manifested in the curd when its woolly appearance changes
and assumes the character of small, hard, and transparent globules. This

condition can be corrected by adding some water and boiling the water well through the mass.

Instead of the somewhat haphazard method of salting-out described, a more rational quantitative method can be employed. Salting-out should be carried out in the manner explained in the appendix for experimental boils. The exact quantities of material involved in the operation can be ascertained at any moment if the weight of fats, alkali, and salt charged into the kettle are known. By the use of the manometric weighing gage, the total weight of the mass in the pan can be ascertained easily. The difference between the known weight of the charge and the total weight of the pan contents expresses, at any moment of the operation, the weight of water added or condensed.

After the lye has settled out and run off, the weight of the curd can be taken with the help of the gage and the "efficiency" of the separation calculated (see Chapter XVII, Section 3).

(c) *Additional Changes or Washes.* Whenever it has been decided to apply one or more additional washes for any of the above mentioned reasons (further purification of the soap, recovery of glycerine, etc.), they should be carried out according to a definite plan.

As an example for such a plan the countercurrent procedure cited in Chapter XVII should be considered. In the case referred to, 6 tons of fatty acids were saponified and grained-out with such amounts of water and salt that 10 tons of soap separated from 8.15 tons of lye. The experiment having been made with tallow, it is to be presumed that the lye contained about 7% salt. The lye, consequently, consisted of 570 kg. of salt and 7.58 tons of water plus glycerine. After the 8.15 tons of lye had been drawn off, it was decided to establish again the same proportion between curd and lye in the second wash. The only thing to do was to weigh the first curd, and when its weight was correctly found to be 10 tons, to add 8.15 tons of lye containing 570 kg. of salt to the kettle. After sufficient settling time the weight of the resulting curd was again approximately 10 tons. In the third wash, according to plan, only 3.5 tons of lye had to be separated. Consequently, to the 10 tons of curd in the kettle, a solution of 245 kg. of salt in 3255 kg. of water had to be added.

Here, again, dry salt or brine could be used. Calculation with dry salt is, of course, simpler. When brine is used, it may be calculated from its saturated solution which contains 26% salt. Calculated for brine, the lye consists of 942 kg. of brine and 2558 kg. of water, the formula for calculation being:

$$\text{Amount of Brine Necessary} = \frac{100x \times \text{Dry salt}}{26}$$

The salt solution should be boiled through with the previous curd by open steam before being allowed to settle. Prolonged boiling, of course, could cause the dilution of the mass with condensed water and upset the graining

process. At the end of each wash, care should be taken that the lye or the soap produces a slight bite or that it contains sufficient free caustic to tint thymolphthalein paper pale blue.

(d) *Finishing curd or "Boiling Clear."* The curd finished by salting-out in the normal way does not yield a soap with suitable marketable properties. The most efficient curd—even after prolonged settling, and containing the minimum of entangled lye—would produce, on solidifying, a brittle, foamy, softish cake of unsuitable consistency. In order to avoid this, the soap mass must be boiled for a prolonged period, before the salting-out takes place, until the foamy appearance of the mass disappears or, as is done in most cases, the curd must be boiled through in the lye after the formation of the curd by graining has been accomplished. In European practice, the latter process is called *boiling clear.*

Boiling clear is carried out with the open steam coil shut and heating with direct fire only, or, in modern plants—with a closed steam coil. At the start, the lye concentration is equal to or slightly higher than the corresponding L.L.C. of the fat charge. As a result of this boiling a number of phenomena take place simultaneously. First, the air bubbles attached to the soap globules are detached and driven to the surface, where they form a foamy layer which slowly dissipates during the prolonged boiling. As a result of this, the volume of the pan contents increases considerably, and in order to ensure sufficient space it is sometimes necessary to eliminate part of the lye.

With the disappearance of the foam, the color of the curd becomes darker and more translucent, and the individual soap globules acquire a tendency to liquefy on standing, thus producing a soap aggregate of much more uniform character than when the soap is prepared without the boiling clear operation. Covered kettles should be used during this operation or the kettle should be covered temporarily with wooden boards in order to have the surface well under steam; when, because of the rising of the foam layer during the boiling, the danger of the kettle boiling over becomes imminent, the attendant may open one or two of these boards to enable him to agitate and cool the surface with a paddle.

The end of the boiling clear operation can be detected by the clear and darkened appearance of the soap globules as well as from the manner in which the boiling proceeds. At this stage, the mass becomes so dense that the steam breaks through the surface with great difficulty. Simultaneously with the process of foam elimination, a gradual concentration of the lye takes place. It is the proper control of this concentration process on which the whole act of the boiling clear depends. In fact, when looking through the literature, quite divergent views are found as to the proper final concentra-

tion to which the boiling should be pushed. Ubbelohde and Heller[7] mention an example of a tallow soap which has been salted out on a lye containing: NaOH 0.96%, Na_2CO_3 0.82%, NaCl 5.34. The corresponding soap had the following analysis:

Fatty acid hydrates	57.83%
Na	4.78%
NaCl	1.49%

After the boiling clear the lye contained: NaOH 1.01%, Na_2CO_3 0.93%, NaCl 6.01%. The pure curd, after the boiling clear, had the following analysis:

Fatty acids	57.93%
Na	4.72%
NaCl	0.15%

It is remarkable that, although the lye had been concentrated only to an extent of about 10%, the electrolyte contents of the soap had fallen in the course of the process to about one-tenth of the electrolytes originally present in the grained curd.

In other instances, authors mention a far higher ratio of concentration as desirable when boiling clear. Davidsohn[7a] states: "The lye should have, in the hot state, a concentration of 16° Bé. Should the concentration remain below that strength, it is advisable to add to it some salt or brine. A concentration over 18° Bé should be lowered, however, by the addition of water."

The true purpose of boiling clear is defined by Thomssen and Kemp:[8]

The object of a soap which is finished "curd" or grained, is to obtain a harder piece of goods from a low titer fat or to increase the percentage of fatty acids in the finished soap. This is still another method of producing a cheap grade of soap as by its adoption the cheaper oils and fats may be used to obtain a firm piece of soap.

A typical charge for curd soap is:

Red oil	63 parts
Tallow	10
Rosin	27

Cottonseed foots may be employed in place of red oil and a tallow of too high titer is not suitable for this kind of soap.

The red oil and tallow are first saponified with 15° Bé lye, boiler pressure 80–90 pounds, 18° Bé lye for lower steam pressure, and two washings given to extract the glycerine. The rosin is added at the strengthening change and at the finish the soap is "pitched," that is to say, the soap is settled overnight only. The next day the lyes are drawn off and a portion of the niger pumped to another kettle which prevents later streaking of the soap.

[7] L. Ubbelohde and H. Heller, *Chemie u. Technologie der Seifen und Waschmittel*, Hirzel, Leipzig, 1930, p. 422.

[7a] J. Davidsohn, *Lehrbuch der Seifenfabrikation*, Borntraeger, Berlin, 1928.

[8] E. G. Thomssen and C. R. Kemp, *Modern Soap Making*, MacNair-Dorland, New York, 1937, pp. 254–255.

The soap is then boiled with 18° Bé lye as with another strengthening change under closed steam. Salt brine or "pickle," 15° Bé is then added and the mass boiled with closed steam until the brine reaches a density of 18° Bé, and the kettle pumped the next day. A soap of this type requires either hand or power crutching to assure homogeneity and prevention of streaks. To obviate air spaces it is advisable to place over the top of the frame a tightly-fitted board which is heavily weighed down. This soap is pressed without any milling.

In a way similar to the above, hard soap can be produced from dark refinery foots of low titer. The foots are saponified with 30° Bé caustic and salted with brine. After the lye is drawn off next morning, a new batch of foots is added to the curd, saponified, and salted-out as on the day before.

On the third day, the curd is diluted with water or open steam until the soap floats large bubbles, when a sample is lightly thrown into the air from a paddle. At this stage the soap is finished with as much dry salt as would suffice to form a large quantity of lye, but still containing some niger to eliminate as much color and impurity from the foots as possible.

Next day, after the lye and niger have been drawn off, the remaining curd is well boiled through with open steam and then boiled clear with 35° Bé caustic for about eight hours. The curd becomes clear and dehydrated. The strong lye is drawn off and used for another boil. In order to eliminate the excess caustic from the curd, it is boiled through with 6–7° Bé brine and the lye is allowed to separate again from the curd. The resulting lye measures 8° Bé. This soap, when filled into frames, gives a hard soap of very good consistency and a glossy cut.

(C) Curds of a High Fat Content by Boiling Clear on Strong Electrolyte Solutions

It will be remembered that, in Wigner's opinion, curds richest in soap are produced when the lye on which the curd has been grained-out was low in electrolyte concentration and vice versa. One exception to this rule, also mentioned by the same author, has been cited in Chapter XVII. There seems to be a contradiction between the two statements, but this will be cleared up when we consider the fact that a difference must exist between conditions prevailing during the ordinary salting-out and of boiling clear, respectively, the latter process consisting of prolonged boiling on concentrated electrolytes solution. It is obvious that during long hours of boiling the system acquires more chances to build up equilibria between lye and curd than would be possible during the short period of graining.

This has been illustrated, for instance, by the example quoted from Ubbelohde and Goldschmidt, in which after the long period of boiling clear on a comparatively weak salt solution, the soap contents of the curd was not considerably raised, but, on the other hand, the salt contents of the curd was reduced to one-tenth of its original value.

Merklen[9] states in his treatise:

Lewkowitch [a well-known British soap technologist] puts the maximum possible fatty acid content of a settled curd at 63 to 64%, and he doubts whether, in any circumstances, a curd could contain as much as 69% of pure soap. Poppyseed oil soap boiled on a lye of 25.5° Bé [in Merklen's own experiments] yielded a curd containing 74% of pure soap and it should be stressed that this value does not represent the maximum percentage of pure soap which a settled curd may contain. The same soap would have yielded an even higher pure soap concentration than 74% provided that the lye on which it had been boiled was still more highly concentrated. In fact, a palm oil soap boiled on a lye totally saturated in electrolytes containing 77% pure soap or 71.2% fatty acids.

See also Table V-2.

We are inclined to form the opinion that soaps produced as a result of prolonged "boiling clear" on concentrated electrolytes solution constitute the same *kettle wax* soap phase which has nothing in common with soaps belonging to the proper neat or curd areas, and it is therefore comprehensible when their physical properties are also different from those finished only by simple salting-out or by fitting.

(D) Neutralization of Alkali in the Lye

In the above description of curd soap manufacture, the necessity of having sufficient caustic in the finishing lye was stressed. Keeping in mind what had been stated on loss standards (Chap. XVII, 2), it is obvious that larger quantities of caustic and also of sodium carbonate left in the lyes must be recovered before the lye is sent into the glycerine department or into the sewer.

Alkali recovery from the lye is carried out by adding to the lye a quantity of fatty acids equivalent to the caustic soda and sodium carbonate contents, and boiling the mixture until soap is formed and eventually floats to the surface, where it may be skimmed off. It is not advisable to use neutral fats instead of fatty acid because the former would only neutralize the caustic soda while unable to react with sodium carbonate. Therefore, the only material that can be used in addition to fatty acids for neutralization of the spent lye is rosin, which contains free abietic acid.

However, it is not advisable to neutralize the whole of the remaining alkali in the lye, as in this case acid soaps would be formed, which—due to their viscous consistency—are likely to enclose impurities from the spent lye. The proper procedure, therefore, would be to determine the total alkali content of the lye prior to neutralization. and to calculate the quantity of fatty acid necessary to neutralize it in such a way that 0.4% sodium carbonate would still remain in the lye. It is obvious that caustic soda is neutralized

[9] F. Merklen, *Etude sur la Constitution de Savon du Commerce*, Marseille, 1906; (a) p. 73, (b) p. 120. German edition, 1907.

before the sodium carbonate, and as a result of this it is always the latter which is left in the neutralized lye.

Example: 10 g. of lye is titrated with 11.2 ml. of 0.5 N HCl against methyl orange indicator; the spent lye contains $11.2 \times 0.0265 \times 10 = 2.97\%$ total alkali calculated as sodium carbonate. Subtract 0.4% from 2.97%, and obtain 2.57% of total alkali for neutralization. This necessitates the use of 13.5 kg. of tallow fatty acids for 100 kg. of lye. If the total quantity of lye is 3250 kg. then $(3250 \times 13.5)/100 = 44$ kg. of tallow fatty acid required for neutralization.

(E) BLEACHING—ANOTHER CHANGE

Bleaching materials are described in Chapter X.

Bleaching is best carried out between the saponification and the finish. Essentially, it is one of the changes and should be dealt with as such.

Consider a reduction bleach, with sodium hydrosulfite $(Na_2S_2O_4)$ as an example. The procedure should be as follows: after saponification, one or two changes for washing should preferably be given. The amount of reducible substances that are removed by the washes determines the amount of chemical that must be used for the bleaching. The problem then occurs of balancing the expenses incurred when carrying out a number of changes as against a larger quantity of bleaching chemical used. In any case, care must be taken that the charge is well saponified, that it contains the normal amount of excess alkali, and that it is brought to the proper "closed" state before the chemical is added.

One part of $Na_2S_2O_4$ is dissolved in 10 parts of cold water, and made alkaline by the addition of 0.1 part of caustic soda of 30° Bé. The preparation is mixed into the well-boiling mass of soap. 1–3 kg. of hydrosulfite is used to one ton of fat in the kettle. It is very important to be certain that the soap in the kettle has a sufficient excess of caustic, otherwise the bleach is destroyed, with the evolution of SO_2.

Sodium hydrosulfite is able to dissolve any traces of iron which may have had access into the soap from iron-contaminated caustic lyes or directly by corroding the steel equipment. Iron is dissolved only by the lye when there is sufficient alkalinity in the soap during the bleaching operation and afterward. At normal conditions, that is, when the total alkalinity of the lye is above 0.4%, the lye has a dark color, but it does not carry dark green and black particles, and the soap bleaches to a pale yellowish tint. However, this is not the case with soap of insufficient alkalinity. In such cases, the soap becomes grey to dark green due to certain organic iron sulfides which cannot pass into the lye under these circumstances.

After a period of about 30 minutes of sustained boiling the reducing substances evolved from the mixture have had ample opportunity for displaying their effect, and the pan can be grained-out as usual. As described, the color-

ing substances and the iron compounds pass into the lye and it is during neutralization of the lye that these substances make themselves felt. At a certain degree of low alkalinity the characteristic smell of sulfur compounds are noted, and also, in most cases, a dark green or black precipitation occurs. Some soapmakers have reported that lyes containing the spent chemical and its derivatives require more careful handling when prepared for glycerine recovery in the glycerine department. Special care must be taken to boil the lye for a time in the acid state in order to eliminate completely sulfurous acid.

There are certain naturally colored soaps which can be bleached quite quickly by these reduction chemicals. However, since in most cases the dye in the soap loses its color only temporarily as a result of chemical reduction and since this reaction is reversible, the color generally reappears when the soap is left in contact with the air. This is, for instance, the case with cotton oil soaps produced from crude cottonseed oil, or from cottonseed oil refinery foots. As a rule, bleaching with reducing chemicals alone does not give satisfactory results, as the surface of the soap rapidly regains its dark color and only the deeper layers retain the effect of the bleach.

This kind of bleach can be used on any type of soap, since it does not add any odor to the product, which is the case in certain soaps when bleached with chlorine. It should also be emphasized that this kind of bleach is suitable for light-colored soaps only, and especially for the elimination of iron contamination.

The chlorine bleach is an oxidative reaction. The various methods for preparing chlorine bleaching lye and its mode of action have been described in Chapter X.

The bleaching of curd soap with hypochlorite lyes is carried out with well-diluted bleaching lyes (as a rule, they contain about 4% available chlorine) on a well-closed soap and at a comparatively low temperature. The effect of the hypochlorite lyes is based upon the evolution of oxygen gas from the chemical and the gas being well dispersed throughout the soap mass in order to obtain effective contact with each soap globule in the pan.

The best practice is to saponify the darker fats first and to bring them into a closed but mobile and transparent state. The soap is cooled down to 70–80°C. by dissolving some scraping from previous boils in the mass. The hypochlorite solution is now introduced into the mass through a pipe which reaches to the bottom. The hypochlorite then gradually disintegrates at the bottom of the kettle and the oxygen bubbles slowly rise to the top, displaying their bleaching action on their way upward. Bleaching action, as a rule, is completed in one-half to one hour.

It is not possible to give a generally valid estimate as to what amount of

bleaching solution is needed.   However, it is good practice to make small laboratory tests from which the operator can derive the approximate quantity of bleaching solution to be prepared for the large batch.

It is self-evident that a curd purified by several washes lends itself to better and quicker bleaching and necessitates the use of less chlorine to produce the same effect than a soap which previously had not been treated at all. The impurities of the spent lye naturally consume considerable amounts of chlorine, which could be economized if the dirty lyes were drawn off prior to the bleaching operation.

Soap from cottonseed foots is totally discolored when bleached with sufficient amounts of hypochlorite solutions, and the color does not reappear, even after prolonged storing of the soap.

A serious disadvantage of this kind of bleach is that certain kinds of soaps retain the odor of chlorine.   This is especially true of soaps containing coconut oil, since it seems that with these soaps some chemical action between the soap and the bleaching material takes place.

After bleaching with hypochlorite solution, it is essential to grain the soap. not only in order to finish it in the ordinary way, but also to eliminate the odor of the bleaching reagent.   Any trace of chlorine can be detected by a test with starch-iodide test paper, which turns blue if chlorine is present.

The bleaching effect of hypochlorite is considerably reduced when the charge contains rosin.

(F) THE ROSIN CHANGE

Rosin is an excellent raw material for use in soap changes.   It is cheap, imparts plasticity to the soap, enhances lathering, and protects the soap to a small degree against rancidity.   During saponification and graining, however, it does not behave like other fats.   This difference in behavior is due to the fact that rosin contains no fatty acids, but consists largely of abietic acid, which is present in rosin in the free state.   Consequently, rosin can be treated as a free fatty acid and saponified with cheap soda ash.   Rosin soap is very susceptible to electrolyte action and, when salted-out by small quantities of salt, this soap, contrary to fatty-derived soaps, settles to the bottom.   The lye does not contain any glycerine, of course.

Because of these differences between the behavior of rosin soap and other kinds of soap, some soapmakers feel that it is advisable to prepare the rosin soap in a special change which should take place as the last change before the fit.   At this stage the glycerine has already been recovered from the soap by the previous washes and, owing to the circumstance that rosin does not contribute any glycerine to the spent lyes, the glycerine-free lyes may be discarded.

In some countries it is usual to saponify and salt-out the rosin in a special vessel and to pump the purified rosin soap into the main kettle just before fitting is started.

In Europe, the rosin is used to neutralize excess alkali in the spent lye.

(2) Manufacture of Neat Soap Settled on Niger

The theoretical principles of the formation of neat soap and niger are discussed in previous chapters, and the small-scale experimental production of this kind of soap is described in the appendix..

It is not known when and by whom it was discovered that partial salting-out of a soap solution through addition of water produced two separate layers, one of which consists of pure neat soap of higher quality than either ordinary or boiled-clear curd soap. It seems quite probable to us that this happened when the raw materials like coconut oil were introduced into soap-boiling technique. The soaps of these fats or their mixtures with other fats are difficult to salt-out completely, and in order to reach their L.L.C. it is necessary to use highly concentrated lye.

While experimenting with varying lye concentrations the observation must have been made eventually that in a region before the L.L.C., that is, when total salting-out has been reached, a system was formed in which the lower layer was not a clear lye, but a soap solution of more or less high concentration. The lower the lye concentration remained below the ultimate L.L.C., the richer in soap was the lower layer and the smaller the upper layer of good soap. But the final most important observation made was that the smaller the top layer of good soap, the better was the quality of soap in every respect: in regard to electrolyte content, consistency, and also detergency. A means of refining the soap quality by careful adjustment between the quantities of both layers was found.

Lederer[10] expresses this in the following terms: When an electrolyte has been added to a soap solution in such quantities that the "threshold concentration" has been passed, but the L.L.C. not yet reached, we get a separation into three layers, as represented schematically in the Appendix. This process is called "partial salting-out." According to the concentration of the soap solution prior to salting-out, the relative quantities of the layers vary within wide limits. With highly concentrated soap solutions (about 50%) and electrolyte concentrations about one-half per cent higher than the threshold concentration [it is noted that Lederer uses here the term *threshold concentration* in the same sense as Kawakami defined *limited fitting concentration*], a three-layer system is obtained consisting of a small amount of clear lye,

[10] E. L. Lederer, *Kolloidchemie der Seifen*, Steinkopff, Dresden und Leipzig, 1932, p. 289.

about one-third volume of niger, and more than half of the total volume pure
neat soap. These proportions are approximately the same as those regarded
as normal when soap is produced by the process of fitting neat soap on niger
in practical operations.

It may be stated roughly that the soapmaker regards it as a good standard
yield when he succeeds in cleansing two-thirds of the fat charge employed as
good neat soap, leaving one-third of the fat in the kettle as niger.

The system of neat soap on niger can be established either by adding
insufficient electrolyte for total salting-out to a soap solution, or by adding
sufficient water to a normal curd for dissolving some of the soap and for
causing its separation into two layers. Thus, there are two methods in use
for the production of neat soap. The first is called the *direct* and the second
the *indirect* method.

The direct method for the manufacture of fitted or settled soap is generally
employed when the fat charge is sufficiently pure or when, for some reason
or other, the purifying of the less pure part of the fats has been carried out
separately. An example is the case mentioned in Ch. XVII, Sect. 3E, where
the fats of lower quality (refinery and soapery foots) have been saponified in
a separate kettle and pumped, after having been purified by several washes,
into the main kettle, in which only saponification of the pure quality coconut
oil has taken place. To finish the neat soap directly without having purified
the fat charge by several washes before the fitting operation would mean that
only a part of the impurities would go to the niger, a large part of them being
retained by the neat soap.

(A) THE CURD SOAP

The curd soap must be well prepared before the fitting operation is started.
This is done by conducting the whole process through all the stages described
as part of the manufacturing method for curd soaps, that is, saponification,
several washes for purification, and glycerine recovery. The boiling clear on
concentrated lyes is not necessary in this case, but bleaching may be added
when the fat charge contains exceptionally dark ingredients.

The following fat charges are in use for the manufacture of fitted neat
soap settled on niger. The soaps produced from these charges are generally
sold as household or laundry bar soaps:

(a) 40% tallow
     40% palm kernel oil
     20% rosin
(b) 30% lard
     70% coconut oil
(c) 40% hardened oil
     50% coconut oil
     10% rosin

(d) 30% peanut or cottonseed oil
     55% coconut oil
     15% rosin
(e) 20% cotton oil, neutralized
     60% palm kernel oil
     20% rosin
(f) 40% palm kernel oil
     40% distilled cotton oil fatty acids
     20% rosin

(*f*) 70% coconut oil
      30% rosin
(*g*) 40% palm kernel oil
      40% sunflower oil
      20% rosin
(*h*) 40% bleached palm oil
      40% coconut oil
      20% rosin
(*i*) 20% peanut oil
      40% bleached palm oil
      40% palm kernel oil

(*j*) 15% hardened oil
      15% lard
      10% cotton oil, neutralized
      15% tallow
      45% coconut oil
(*k*) 30% cotton oil, neutralized
      20% tallow
      50% palm kernel oil
(*l*) 50% coconut oil fatty acid
      35% peanut oil fatty acid
      15% rosin

(B) SAPONIFICATION GRAINING PROCESS AND THE FAT CHARGE

The saponification process is carried out in the same way as with curd soaps, the only difference being that in the present charge there are considerable amounts of fats which are not very susceptible to the separating action of lyes. It is therefore possible to saponify these charges with even more concentrated caustic lye than is possible with charges containing only tallow, peanut oil, or olive oil. On the other hand, the salting-out of the charge for glycerine recovery or purification must be made with the greatest of care. This is because the L.L.C. of mixtures containing large quantities of coconut oil or palm kernel oil is quite high.

Let us consider some exact figures reported by Merklen.[9b] A mixture of equal parts of coconut and peanut oils was saponified and the lye diluted until a point was reached when soap started to dissolve in the lye. The analysis of this lye was:

Density at 18°C.	23° Bé
Na_2CO_3	1.94%
NaOH	3.51%
NaCl	16.70%
Glycerine	4.00%

This lye can be diluted down to 20° Bé without larger quantities of soap being dissolved, but with further dilution soap would start to dissolve in large proportions.

Now it is obvious that the curd separating on a lye of such high concentration is not very efficient and retains considerable amounts of entrained lyes. Consequently, it contains large quantities of electrolytes. In order to eliminate the glycerine from such soaps, it is necessary to work with large ratios of lyes which make the recovery uneconomical. For example:

Theoretically, coconut oil produces about 14% of its weight in glycerine, peanut oil about 10%; a 1 : 1 mixture of both consequently produces 12%. Let us consider the quantitative example from Ch. XVII, 3 D. 60 kg. of fatty acids (63 kg. of neutral fats) containing 12% glycerine produce, after saponification, 7.2 kg. of glycerine. These

7.2 kg. of glycerine must be contained in 180 kg. of solution in order to produce a 4% glycerine lye. 60 kg. of fatty acids is equivalent to about 65 kg. of pure soap. The total weight of the soap in the pan must have been $65 + 180 = 245$ kg. prior to the separation of layers. The soap solution contained, at the moment of separation, $(100 \times 60)/245 = 24.5\%$ fatty acids, which is an extremely high dilution for salting-out. The ratio between fatty acids and lye separated is $60 : 80 = 1 : 3$, which does not allow for a good production standard per unit of kettle space.

However, the reconstruction of the condition under which Merklen conducted his experiment was made under the presumption that he carried out one wash only. This is by no means certain. But should he have divided the lye bulk into two washes with a ratio of $1 : 1.5$, his results with respect to glycerine recovery would have been even worse, due to the fact that two inefficient curds influence the glycerine recovery more unfavorably than one.

In any case, a curd in equilibrium with a lye of a concentration as high as the above must contain large quantities of electrolytes and its fitting will certainly cause difficulties.

This is why coconut oil or palm kernel oil cannot be used alone for the manufacture of settled soaps. The high stability of these soaps against electrolyte solutions would necessitate their being salted-out or fitted with salt solutions of a very high concentration. These soaps, under such circumstances, would adsorb very high quantities of electrolytes, salt, and caustic soda, and both would cause the soap to display inferior qualities.

It must be remembered that it is also difficult to make fitted soaps from fat charges which do not contain any coconut or palm kernel oils. This is not only because of the lack of lather in such soap, but also because of the interval between the concentration of total salting out (L.L.C.) and the concentration of fitting (F.L.C.). If we take, for example, the figures of Merklen for sesame oil soap: L.L.C. is found to be 9° Bé, fitting must be carried out at 7.5° Bé, the interval is 1.5° Bé. It is extremely difficult, especially when working with the direct method, to add the suitable amount of salt gradually without surpassing the limit after which total graining would occur, or alternatively to remain below it and thus cause large quantities of soap to dissolve in the niger.

With a mixture like the above, of 1 part of coconut oil to 1 part of peanut oil, working becomes much easier. The L.L.C. in this case is 23° Bé, whereas fitting is carried out at 18.5° Bé, the interval between them being 4.5° Bé, giving a much better chance to the operator to find the proper concentration, and to ensure good separation between neat and niger.

Summing up, it may be stated that settled soap for household or laundry purposes (not for toilet soap bases) should contain at least 30% of soaps nonsusceptible to electrolytes of the type of coconut oil, palm kernel oil, or babassu fat. When using liquid oil only in conjunction with these fats, it is sufficient to combine 55% of coconut oil with these oils, even when up to

10% of rosin is present in the fat charge. This applies to summertime, whereas in the winter 45% of coconut oil would do as well. Palm kernel oil produces somewhat softer soaps than coconut oil, and this is why, when working with the former, its proportion in the fat charge is higher than prescribed for coconut oil. Tallow or hardened fat can take the place of coconut oil in the fat charge as far as hardness only is concerned. However, it must be borne in mind that by reducing the proportion of coconut oil in the charge the lathering properties of the soap suffer unavoidably. On the other hand, soap containing a certain proportion of tallow or lard behaves more economically in the laundry. Tallow soap generally has better foaming properties than most of the high titer hard fats.

(C) DIRECT METHOD OF FINISHING NEAT SOAP ON NIGER (THE FITTING PROCESS)

After the saponification of the charge and after sufficient changes for the elimination of glycerine have taken place, the soap is brought to the closed, homogeneous state, and the final alkali content regulated by addition of some caustic to the mass which, at this stage, should contain 0.3–0.6% caustic soda. The soap is again tested by kneading a sample between the fingers. The sample should have the proper consistency on cooling to indicate that no unsaponified fat is present. The mass should now boil easily and uniformly in the kettle. At this state, the addition of small batches of dry salt or brine should be started. Each addition now changes the state and aspect of the boiling soap. In order to keep these changes under control, the following tests may be carried out after the addition of each batch of salt, and, after the salt, by sufficient boiling, has been given the opportunity of displaying its action.

(a) The soapmaker throws a small amount of the hot liquid soap up into the air by taking some of it directly from the boiling pan on his paddle and launching it with a quick movement over the kettle surface. There are only a few bubbles or, if they are small and bursting too quickly, then the soap does not contain sufficient water to be mobile, apart from the fact that niger of suitable composition is not yet formed. Water or salt or both must be added until large bubbles are readily formed with the throw-test and these large bubbles flutter slowly above the kettle surface. These fluttering bubbles are produced only when niger is already present in the kettle containing the proper amount of soap.

(b) The kneading test must show the proper consistency, that is, the soap should neither be too short nor brittle nor greasy when worked between the fingers.

(c) The wooden paddle is heated by keeping it in the hot mass for a few minutes. The withdrawn paddle covered with soap is held flat over the kettle for a short time and then inclined. The soap should run down in small plates and leave the paddle covered with a thin transparent layer of niger which becomes turbid and white when it cools.

(d) The pan contents are well boiled through with steam and a sample of about one quart is withdrawn with the aid of a scoop. The sample is poured into a beaker and left alone for settling in a warm place, or even better, in a boiling water bath. Separation of this sample takes place quite quickly and the layers can be distinguished sharply.

The niger is dark, slimy, and produces threads between forefinger and thumb. It forms a jelly on cooling, which releases some clear lye when pressed. The niger should be strongly alkaline. The neat soap settling as upper layer should have a fair color and, when kneaded between the fingers, should have a dry consistency when cool and produce only short threads when tested hot.

(e) The attendant should observe the boiling surface of the mass. Here also the mass "boils in plates," as described in Section 1 for the finishing of curd soap. The squares are separated by white, rather pointed, edges or furrows. Dark patches appear in these furrows, indicating that the separated dark niger is launched from beneath onto the surface. Some soapmakers maintain that the dark patches are produced at the moment when the niger starts to separate from the neat soap. The aspect of the surface also tells the soapmaker something about the proper alkali content of the soap in the moment of fitting. With proper excess of alkali the squares are covered with a film or membrane of soap which can be removed by a sweep with the paddle, revealing the fresh glossy soap surface. The furrows must show a characteristic glossiness as well. When the proper alkalinity is lacking, the squares and furrows resemble a dimmed varnished surface.

Too much electrolyte causes too large an upper layer to separate. Such soaps are then quite similar to the curd soaps produced without the boiling clear process and, consequently, they may show some *feather*, which is an undesired property in modern neat soaps. Such soaps may also separate some liquor when stored and, as a further consequence, they may later become covered with a white precipitate. When insufficient amounts of salt have been used, the yield of neat soap is too small. Of course, this practice is uneconomical. In such cases, the separation of niger and neat soap proceeds with difficulty due to the fact that the specific gravity between niger and neat becomes less marked.

Here are some quantitative examples showing the ratio of settling when neat soaps on niger are produced by the direct method.[11]

(a) The fat charge amounted to 2500 kg. and contained 60 parts of palm kernel oil fatty acids and 40 parts of tallow. The charge was dark and had to be given a fine fit with weak salt solution in order to obtain a good degree of purification. As a result, about 2500 to 2650 kg. of good neat soap was produced from the above charge. The higher figure represents a fair normal yield (2/3) of the fat charge obtained in form of good neat soap and 1/3 in the niger), while the smaller figure is to be looked upon as an uneconomical yield. The niger weighed 3000 to 3100 kg. and, on graining, produced curd weighing between 1100 and 1250 kg. The lye weighed 1900–2000 kg. On the whole, the method employed cannot be regarded as economical, as the kettle space could not be utilized to a sufficient extent due to the weak salt solution and the large volumes of niger produced. This is a disadvantage of the direct method. By employing the indirect method, the volume of niger could have been restricted to more reasonable proportions. This example shows the unsuitability of the direct method for the manufacture of light-colored soaps from dark fat charges, when no washes or a bleaching change were given prior to the partial salting-out.

(b) The fat charge consisted of 2125 kg. of palm kernel oil fatty acid, 375 kg. of light-colored extracted bone fat and 500 kg. of rosin—altogether 3000 kg. 3450 to 3750 kg. of good neat soap on 2050–2850 kg. of niger was produced. The niger separated into 750–1050 kg. of curd and 1300–1800 kg. of lye. The higher lye bulk values came

from batches in which large quantities of settings from previous boils had to be utilized, due to which large amounts of condensed water were introduced in the kettle with the solution of these parts of the charge. In this instance, even the lower value represents a good yield, and the lye-bulk is considerably lower, although the fat charge was higher than in the example quoted first. The better yield and the more favorable lye bulk is due to the fact that in the second case the fat charge, being of better color, was more suitable for the direct process.

The figures of Table XVIII-1[11] are the result of analyses of the neat soap and of the corresponding settled niger in a well-conducted soap factory. It is instructive to study such figures, since they might teach the soapmaker to

TABLE XVIII-1

ELECTROLYTE DISTRIBUTION BETWEEN NEAT AND NIGER
IN A COCONUT–PALM KERNEL TALLOW SOAP[11]

Electrolyte	1		2		3	
	Niger	Neat	Niger	Neat	Niger	Neat
NV	—	236.4	—	226.7	—	230.2
NaOH	1.44	0.06	1.32	0.07	1.52	0.06
NaCl	4.12	0.62	5.12	0.64	2.76	0.39
FA	—	61.7	—	62.1	—	62.9

Electrolyte	4		5		6	
	Niger	Neat	Niger	Neat	Niger	Neat
NV	—	231.0	—	232.2	—	229.6
NaOH	1.06	0.06	0.96	0.06	1.32	0.18
NaCl	3.18	0.54	1.58	0.44	1.19	0.31
FA	—	61.4	—	59.4	—	62.4

judge the electrolyte concentrations to be expected in the soap when cooling under controlled and defined conditions. The first six examples contained coconut or palm kernel oils with some tallow in proportions as indicated by the neutralization value given in each case. Charges with the higher neutralization value contained larger quantities of coconut or palm kernel oils.

The examples of Table XVIII-2[11] show the distribution of electrolytes between neat soap and niger when the fat charge contained 75 parts of palm kernel oil and 25 parts of rosin.

In this matter of electrolyte equilibrium between neat and niger, most interesting material can be found in the classical works of Merklen on this problem. The reader is referred to Table V-2. The methods used by Merklen in his fitting experiments was, however, the indirect method (see also Part A).

[11] L. Ubbelohde and H. Heller, *Chemie u. Technologie der Seifen und Waschmittel*, Hirzel, Leipzig, 1930, pp. 430, 433.

(D) INDIRECT METHOD OF MANUFACTURING NEAT SOAP ON NIGER
(CONSIDERATION OF GLYCERINE YIELD)

This method is suitable for fat charges containing dark and impure fats. Nowadays, there is almost no soap factory where household soaps are boiled entirely from neutral oils directly as they are produced in the oil mill. Most of the large soap plants are attached to vegetable oil refineries where large amounts of refinery foots and soapstocks are produced, and it is one of the unpleasant jobs of the soapmaking department to utilize these impure materials. When soapstocks are not directly utilized in the company's own soap department but are put on the market, it is not the soapstock as such, but the split and sometimes distilled free fatty acids that are sold.

Coconut and palm kernel oils are generally purer than the other ingredients of the fat charge, and it is for this reason that these two ingredients of the fat charge are usually saponified in two different portions.

TABLE XVIII-2

ELECTROLYTE DISTRIBUTION BETWEEN NEAT AND NIGER
IN A 75% PALM KERNEL OIL–25% ROSIN SOAP[11]

Electrolyte	1		2		3	
	Niger	Neat	Niger	Neat	Niger	Neat
NV	—	225.7	—	227.7	—	223.7
NaOH	1.76	0.12	2.08	0.22	0.44	0.03
NaCl	2.63	0.33	1.87	0.27	3.40	0.65
FA	—	62.3	—	61.3	—	62.1
Water	51.8	—	52.5	—	49.2	—

There are a few problems connected with this procedure. The first is the proper disposal of the curd produced from the niger. This question is dealt with elsewhere, but is touched upon here because the kettle plan is concerned with the salted-out niger. The niger is generally left in the pan where the settling and salting-out have taken place. It is logical to start the saponification process by pumping some of the impurer fats, foots, or soapstocks on top of the grained niger, thus utilizing the excess alkali in the niger. The rosin could also be saponified at this stage by making use of the sodium carbonate present. The presence of a certain proportion of coconut or palm kernel oils in the composition of the niger curd is always of value, since during the subsequent saponification this will help to keep the soap in a closed state. One or several washes should be applied in order to eliminate the glycerine from the charge and also to obtain the required purifying effect. Boiling clear is unnecessary in this case.

When satisfied that the more impure part of the charge has received its proper treatment in this way, some concentrated caustic of 25–30° Bé is

added to the soap, and at this point the coconut or palm kernel oil is pumped into the kettle in small batches. The reaction between lye and coconut oil may become quite violent; care must be taken that the mass does not boil over. The addition of caustic should be regulated in order to have an excess of about 0.5% NaOH in the total kettle contents at the finish.

At this point, a new problem arises in connection with the glycerine content of the added coconut oil. If it is assumed that the coconut oil was added in the form of neutral oil and not as free fatty acid, the whole of the glycerine of the coconut oil would be present in the last change. If at this point finishing is carried out by the direct method—that is, by adding small quantities of salt directly to the homogeneous soap solution as produced by the saponification process, until neat soap or niger has been formed—then this considerable amount of glycerine would be retained by neat and niger. Examples follow:

TABLE XVIII-3

CALCULATION OF GLYCERINE RECOVERY IN THE FIRST CHANGE

	Weight, tons	Water + Salt, tons	FA, tons	Glycerine, tons	Glycerine	
					% in each item	recovered, % total glycerine
Total soap mass	23	9.5	11.3	0.770	3.34	100
Neat soap	12	3.0	7.5	0.243	2.02	31.6
Niger	11	6.5	3.8	0.527	4.79	68.5
Niger curd	5.2	1.5	3.12	0.122	2.34	15.8
Spent lye	5.8	5.0	0.68	0.405	6.98	52.6

In a soap-boiling pan of about 30 cubic meters gross kettle space, soap is produced by pumping purified soap from soapstocks, foots, and rosin containing 6.1 tons of fatty acids into the pan, and saponifying 5.5 tons of coconut oil on top of this soap, thus adding soap containing another 5.2 tons of fatty acids to the total pan content. The pan now contains 23 tons of soap, including 11.3 tons of fatty acids. The pan also contains 770 kg. of glycerine produced from the 5.5 tons of coconut oil on saponification. The 23 tons of soap solution is now fitted by the direct method, and is separated into two layers: 12 tons of neat soap containing 7.5 tons of fatty acid, and 11 tons of niger containing 3.8 tons of fatty acids. The niger is salted-out in such a way that some of the impurities remain in the lye. 11 tons of niger yield 5.2 tons of niger curd containing 3.12 tons of fatty acids and 5.3 tons of spent lye with about 0.68 ton of dark fatty acids in soap form.

With the direct method of finish, the neat soap contains about 2% glycerine and carries with it about 31.6% of the total glycerine and only 52.7% of the total glycerine is recovered in the spent lye, while 15.7% is carried further with the niger curd into the next batch.

What happens to the glycerine from the niger curd and added coconut oil when building up a new charge on the niger curd of the first one? The new fat charge is built up as shown in Table XVIII-4.

On the assumption that the same soap and electrolyte concentrations are used, the

TABLE XVIII-4

BUILDING UP OF THE NEW CHANGE

Fatty acids from niger curd	3.12 tons containing 0.122 ton glycerine
Fresh coconut oil fatty acids	3.76 tons containing 0.560 ton glycerine
Purified foots, etc., fatty acid	4.42 tons
	0.682 ton glycerine

same respective amounts of the different layers—neat soap, niger, niger curd, and lye—are formed. These layers consequently also contain the same amounts of water and therefore the distribution of glycerine takes place according to the percentage ratios laid down in the last column of Table XVIII-5. In order to obtain the amounts of glycerine now present in the various layers multiply the quantity of total glycerine present (0.682 ton) by each of these items.

The neat soap still contains 1.7% glycerine, but the ratio of loss through the neat remains what it was: 31.6% of the total glycerine. The glycerine content of the lye becomes somewhat lower.

The following kettle plan leads to better results. The niger curd contains 1.44 tons of coconut oil fatty acid and 1.68 tons of other oils; saponify on top of it 3.76 of fresh coconut oil (calculated as fatty acid); total 6.88 tons. In this mixture, 75% of coconut oil fatty acid is present and such a charge can be salted-out completely with a lye below 23° Bé.

Even in case of an inefficient curd containing only 59% of fatty acids, the curd weighs no more than 11.6 tons, carrying about 4 tons of total entrained (occluded) lye. Let us regulate the total weight of the soap mass in the kettle to, say, 19.6 tons. The ratio between spent lye and total entrained lye is 8 : 4 and consequently 33% of the glycerine remains in the curd and 67% goes to the lye. 67% of 0.682 ton amounts to 0.456 ton. The spent lye thus contains 5.7% of glycerine. The curd contains 0.225 ton glycerine, or 1.94%. But this curd is not the final product, it can then be finished by the indirect method.

The curd contains sufficient amounts of electrolytes due to the high electrolyte concentration with which it had to be salted-out. All that needs to be done is to make sure that the curd contains a sufficient amount of excess caustic soda, and then to add the other part of the fat charge from the purified soap containing 4.42 tons of fatty acids. This also amounts to 7.5 tons of soap. Altogether there is in the pan $11.6 + 7.5 = 19.1$ tons of soap curd. Depending on the electrolyte content of this soap mass, a certain amount of water must be added, and probably also some electrolytes, until the separation into the same proportion of layers, as described in the former example, is obtained. On

TABLE XVIII-5

DISTRIBUTION OF LAYERS AND OF THE GLYCERINE THEREIN
IN THE SECOND CHARGE

	Weight, tons	% total glycerine in the layer	Glycerine, tons	% glycerine in each item
Neat soap	12	31.6	0.216	1.80
Niger	11	68.5	0.467	4.25
Niger curd	5.2	15.7	0.108	2.08
Spent lye	5.8	52.7	0.359	6.19

the assumption that there is again 23 tons of total soap and the same proportion of neat soap and niger, the final neat soap now contains only 31.6% of 0.225 ton, that is, 0.071 ton glycerine, which means that the neat soap now contains only 0.39% of glycerine, and the spent lye 0.118 ton of glycerine, or 2.04%. This figure becomes even more advantageous with the next batch, as the niger curd now carries over only 0.039 ton of glycerine instead of 0.122 ton.

It is possible to produce more soap per unit kettle space per week when employing the direct method, that is, by fitting directly without any previous salting-out operation, however the decision to follow this method will depend on circumstances.

(E) The Fitting Process with the Indirect Method

The phenomena underlying the fitting process are considered in Part A and in the appendix dealing with laboratory soap boiling. The fiitting process has been described in detail.

By adding water to the pan we depart from the conditions in which curd as such is able to exist. The more water or weak salt solution that is added, the larger becomes the niger layer and the smaller (but finer in texture) becomes the layer of neat soap.

The soap is now tested with the paddle by the bubble flutter test. While proceeding with the direct method (Section 1, B), we started with a closed soap solution and opened it by addition of salt. There is was noted that the soap, when still in the closed state (which is a result of electrolyte deficiency), did not produce fluttering bubbles readily. The same is the case when fitting by the indirect method.

When the proper amount of niger has been formed, bubbles should be formed with ease which, after having fluttered in the air for a short time, should burst there and not fall back intact. One expert describes this by advising that the quantity of added water should be the amount the soap requires for sufficient mobility and that the bubbles formed should be of the size of a fist, totally transparent, and not milky, and should burst at once after their formation in the air.

To observe the appearance of the trowel when withdrawn from the boiling mass, some soapmakers use a wooden paddle, some an ordinary mason's trowel, which is easier to clean. When using a wooden instrument like a paddle, care must be taken that no lye or salt is soaked into the wood, or false results may be obtained. Should the soap now run off the trowel in large, thin, coherent plates, instead of in more compact flakes, some salt should be added in order to open the soap slightly. It will be found that, in such cases, the trowel remains covered with an over-all layer of soap solution which solidifies into a soap film. After some concentrated salt or lye solution has been added and the pan boiled with steam, the trowel test is repeated. With the accurate amounts of electrolytes in the kettle the soap runs in thin

flakes of the size of a small visiting card. In the first moment it looks as if the trowel is completely covered by a glossy soap film, but a few seconds later it can be seen that even this thin secondary soap film bursts and the trowel, in patches, becomes bare and dry. The size of these "dry patches" on the trowel or paddle indicates the degree of separation caused by the electrolytes in the kettle, and the proportion in which the neat soap will separate from the niger.

If the dry patches become too large or a drop of clear lye appears at the lower corner of the trowel or paddle, it indicates that the electrolyte addition has been pushed so far that the kettle contains, instead of the two-phase system (neat soap–niger), a three-phase system (neat–niger–lye). Some soapmakers prefer, under certain conditions, to push fitting as far as that. Such a practice certainly makes for a large neat soap yield, but it is up to the soapmaker to decide whether or not this is detrimental to the sales qualities of his product.

Should such a three-phase separation take place accidentally and unintentionally, it can be corrected easily by adding some water or weak solution of 2–3° Bé to the pan. When the fitting procedure is considered finished satisfactorily, the pan contents should be given a last boiling with open steam. With the steam valve well closed (it is advisable to open a blowdown valve) somewhere in the steam line, in order to make sure that no steam leaks through into the kettle), the kettle should be covered and the contents allowed to settle.

It must be expected that, during the last operation, the soap will rise considerably in the kettle. This is due to the contents becoming gradually denser by the addition of water and the formation of niger and neat soap. Under these circumstances, steam under excess pressure is required in order to become able to break through, and this higher pressure raises the surface of the soap. Finally, the bubbles can escape to the surface and there they build up a layer of foam, which will always be found covering the neat soap. When the neat soap is pumped away, there is invariably a scaly formation on the wall of the kettle which had been left there from the foam.

(F) Utilization of the Niger Curd

The niger contains, as a rule, considerable quantities of free caustic soda and sodium carbonate; it is an important task of the soapmaker to recover these valuable materials by neutralization of the niger with rosin or any other free fatty acid. This precipitates the soap, generally in the form of a curd, since soap is more soluble in salt solutions when alkali is present.

The soap is only partially salted-out, however, when the niger is just neutralized, as can be seen by observing the cloudy appearance of the separated lye on the paddle. In such cases, sufficient amounts of dry salt are added

to the boiling niger to correct the test. After a few hours of settling in the kettle, the lye may be drawn off and the niger curd utilized for the next batch.

The niger curd cannot, however, be used repeatedly in indefinite successions without making some provisions, from time to time, for its purification. The impurities of the niger would otherwise be simply returned, to the soap and concentrated there to such a degree that finally only dark and dirty soap would be produced.

Various methods have been devised for the purification of the niger. When two kettles are available, the niger curd should be pumped into the second empty kettle and boiled there with salt water of sufficient strength to eliminate the impurities. After a short settling, the lye can be drawn off, and the color of the lye gives convincing evidence that there had been a great amount of dirt in the niger. The batch may be finished in the same kettle where the cleaning of the niger took place, provided that one or two additional washes were applied to the first one for the complete purification of the niger curd.

In case it is intended to use some rosin in the fat charge, it is advisable to saponify the rosin on the niger and wash the rosin soap along with the niger in the same auxiliary kettle.

It is advisable not to delay drawing off the lye until the next day, otherwise the heavy dirt settles out on the bottom and obstructs the valve and piping; worse still, the dirt may remain in the kettle, while the clear lye is allowed to drain off through the valve. When pumping out the lye, agitation should proceed at the bottom in order to keep the heavy dirt in suspension and give the suction head an opportunity to retain all the dirt from the kettle. If it is not possible, for some reason or other, to eliminate the lye on the same day, then, on the next day, it is advisable to open the direct steam for a short time and stir up the sedimented dirt at the bottom.

Pure salt water should be used for washing the niger. Purified niger is more suitable for bleaching than when still containing impurities. These washings of the niger are important for any kind of neat soap, but they are essential for the manufacture of boiled soap. Toilet soaps produced on impure niger are invariably grey in color.

A second way for purifying the niger is to collect several batches and to finish by fitting and settling on niger. By this method, very efficient purification of the niger may be obtained, since the impurities concentrate in the secondary niger.

Some soapmakers think that it is dangerous to utilize the niger curd for a new boil, since it contains: (a) hydroxy fatty acids, (b) unsaponifiable fat, (c) mucilage, and (d) coloring matter. However, the authors feel that such impurities are not present in a well treated niger to a degree that would warrant discarding.

(G) COMPOSITION OF THE NIGER CURD

In the following example, neat soap settled on niger was produced from: 600 kg. of lard, 900 kg. of tallow, 400 kg. of cottonseed oil. and 1000 kg. of palm kernel oil.

476 kg. of caustic soda was required for saponification. For the "reduction" of the caustic, 100 kg. of sodium carbonate was used. The caustic soda contained 84.05% NaOH and 15.99% Na_2CO_3. The soda ash contained 98.4% Na_2CO_3. For fitting of the soap, 292 kg. of salt was used. The tallow and the lard were saponified with 22° Bé caustic, while half of the soda ash (50 kg.) was added for the maintenance of the proper state of boil. After an hour of boiling in the closed state, the other 50 kg. of soda ash was added, and the amount of caustic necessary for the saponification of the cottonseed and palm kernel oils in the form of 42° Bé solution was measured in. The densely boiling soap now received the proper amount of salt for fitting by the direct method, and was settled overnight. The following were the yields

TABLE XVIII-6

	Fatty acid	
	Of neat soap	Of niger curd soap
Melting point, °C.	41	39
Saponification value	213.5	218.2
Refractive index at 60°	21	18

and analyses of the layers. The neat soap contained 60.84% fatty acid anhydride. The molecular weight of the fatty acid was 257.6. The niger contained 53.88% fatty acid anhydride and the molecular weight was 253.04.

A possible partial reason for the difference between the composition of neat soap and niger is that the soapmaker may not be particularly careful when salting-out the niger. (Oversalting produces inefficient curds containing large quantities of "entrained" lyes.) Another reason for bad curds may be the presence of emulsifiers which cause the curd to retain more water.

The example given also shows that the fatty acids of the neat soap are not entirely identical with those of the niger (compare Chap. V, 3), as indicated by the difference between the molecular weights of the fatty acids in neat and niger.

A second example illustrates this point still further. A toilet soap base with a fat charge of 85 parts of tallow and 15 parts of coconut oil gives the analysis in Table XVIII-6 on neat and niger. With repeated use of the niger, some modification of the fat charge will take place.

(H) Quantitative Fitting Method with the Use of the Pressure Gage

The following procedure is recommended by Wigner:[12]

The rational method [as he terms it] is exactly the same as that described in the making of miniature boils, the only difference being that instead of weighing a beaker of soap on the scales the soap mixture in the pan is weighed by means of a gage. . . .

Suppose, for example, the pan is known to contain 10.5 tons of fatty acids, and the curd to be fitted is found to weigh 18.4 tons (corresponding to 57% fatty acids). Then we say 10.5 tons of fatty acids yields 10.5×1.52 tons of soap hydrate = 16.0 tons [66% rule of Wigner, Chapter V], and the weight of entrained lye, or free solution, is 2.4 tons. The percentage of NaCl in this may be, for the sake of argument, 10.2 [when the salting-out is also carried out by the rational method, as described in the next section, the salt content of the previous lye is identical with the salt contents of the entrained lye in the curd, and is consequently a known value—Au. Note] and from a previous boil it may be found that the desired type of fit is obtained by reducing this to 8%.

2.4 tons of entrained lye with 10.2% salt contains 245 kg. of salt. The quantity of solution containing the 245 kg. of salt will amount to 8%. This is $(2.4 \times 10.2)/8 = 3.06$ tons. Accordingly, the quantity of water to be added for fitting is $3.06 - 2.4 = 0.66$ ton.

The amount of water to be added and the total weight of the pan contents to be obtained for proper and planned fitting are known. Water must now be added, measuring the difference to the final desired weight of the pan contents, in small portions, and boiling up with open steam must follow.

The author of the method just described compared the results which can be obtained when the rational fitting is used with the ordinary empirical methods of the soapmaker. Wigner showed that the appearance of the soap on the paddle is not as reliable for the detection of differences in the yield of soap, etc. as is the method of quantitative measurement and corresponding adjustment of the contents of the pan. It has been found, for instance, that two batches, one yielding neat soap containing 0.5% more fatty acids than the other, nevertheless produced paddle tests of very similar character.

(I) Utilizing the Rational Method of Fitting

It is known from the study of the phase diagram that neat soap is able to exist over a whole range of soap compositions, all of which may be considered as proper neat soap. It was Merklen who explained that it is wrong to assume that genuine neat soap cannot contain less or more fatty acids than exactly 62.5%. The contents of the neat soaps on fatty acids depend on the class of the raw materials used and the way the fitting operation was conducted. This authoritative explanation helped to clear up a very unpleasant legal situation, around the year 1930, when a large number of cases were

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[12] J. H. Wigner, *Soap Manufacture. The Chemical Process*, Chemical Pub. Co., New York, 1940, p. 81.

brought before the courts of Marseilles, all concerning charges of alleged adulteration of neat soaps.

This is one example showing the importance of being able to control the fitting process completely in order to obtain settled soap of the desired composition containing definite amounts of fatty acids.

The expediency of the rational soap fitting process and all that it implies is strongly recommended. The application of such accurate practical methods in soapmaking is in keeping with the great progress made recently in theoretical and experimental studies concerning the phase behavior of neat soap. After learning the existence of a multitude of forms in which soap generally, and neat soap in particular, can exist, it is only logical to endeavor to master the practical methods which permit the production of any particular member of the series.

In Chapter V, 2, the method for studying a fat charge was described, by investigating several of its soap compositions. The analytical data of the experimental series, especially the fatty acid contents in the neat soap and in the niger against salt contents in the free solution, were tabulated and plotted (Fig. V-1). By using such graphs for each fat charge in use at his works, the soapmaker can adjust salt concentration in the free solution in order to obtain soap and niger of any composition within the limits of the desired range.

Here are a few examples given by Wigner for the use of the rational fitting method for the solution of some practical problems in soapmaking:

(*a*) To produce soap, testing 1% less fatty acids, when wishing to comply accurately with a certain fatty acid content prescribed by a contract. This counterbalances the drying loss suffered by the soap before delivery.

(*b*) To reduce fatty acid content in the neat soap, but not by the usual method of a smooth fit which would produce more and richer nigers; instead, it is done by controlled addition of water and salt to a neat soap resulting from a coarser fit. As an example: transformation of neat soap according to sample 3 in Table V-7 into neat soap like sample 8 without increasing the niger and its contents of fatty acids. The problem is to add water to neat soap containing 63.3% fatty acids and 10.7% salt in the free solution, and to form a soap with 61.85% fatty acids and 7.85% salt in the free solution. This can be done only when a certain amount of salt is added along with the water, and the necessary quantities can be easily calculated from the data of the table.

(*c*) For the production of soap powder, a very coarsely fitted neat soap is of advantage. Such a coarse fit can be adjusted by keeping to a high salt concentration in the free solution defined in advance, by experiment, and obtained directly from the chart.

(*d*) Soap base for flakes should be prepared by a coarse fit. Here Wigner clears up a curious confusion prevalent regarding the smoothness of fit versus texture of soaps. Flakes should not contain more than a minimum of salt. One would think that a smooth fit furnishes a smooth-textured soap. However, Table V-7 discloses that neat soap from the smooth fit contains less fatty acids and less salt than soap from a coarse fit. But neat soap for flakes must be dried until it contains 80% fatty acids. By drying the neat soap from a smooth fit to 80%, more water must be evaporated than when doing

the same with a soap from a coarse fit. And so it happens that when the neat from a smooth fit is dried to contain 80% fatty acids, it will have more salt than the soap from the coarse fit which, originally, was richer in salt.

(*e*) For the manufacture of soaps run with silicate solutions, it is preferable to prepare soaps containing less salt. A coarse fit producing soap with a high fatty acid content always contains comparatively less salt than a smooth fit with a smaller fatty acid content.

(3) Boiling of Toilet Soap Base

The manufacture of a high-grade toilet soap involves the production of very pure neat soap settled on niger from raw materials of best quality and a fat charge suitable for producing soap of the required chemical and physical properties. It is mainly on the properties of this toilet soap base that the final quality of the manufactured toilet soap depends.

As to the properties of the soap base which are determined by the soap-boiling method used, it may be stated, in general terms, that neither unsaponified fat nor excess soda should be present over and above a certain standard. The contents in free caustic alkali should not exceed 0.05%. Not more than 0.1% of unsaponified fat should be present. The salt content should be closely controlled and less than 0.5%. Higher salt contents render the toilet soap brittle and subject to cracking.

(A) SELECTION OF RAW MATERIALS

(*a*) *General Principles.* The selection of raw materials should be governed by the following main considerations.

(*1*) The fat charge must contain fats providing sufficient body and consistency, such as tallow and palm oil.

(*2*) The fat charge should contain fats imparting sufficient lathering properties to the soap. These are coconut, palm kernel, and babassu oils.

(*3*) Fats which may be called conditioners in the toilet soap base produce plastic soaps and can be regarded as plasticizers in the soap body. These are lard and certain oils like peanut, olive, or castor oil, which last is occasionally used as a conditioner for lathering properties.

It is essential that these fats should be combined in the proper proportion in order to meet the following requirements: proper feel and plasticity, proper hardness for economy in use, proper solubility and lathering characteristics, proper color and odor, and resistance against rancidity.

It is sometimes difficult to meet all these requirements. Some are seemingly contradictory, such as hardness and plasticity. However, it is possible to combine, for instance, tallow and lard in such a way that the soap will retain a certain plasticity during milling, yet become hard and glossy when stamped and aged. Proper solubility and economy in use, at the same time, can be obtained only when great care is taken in the selection of the fat

charge. Good foaming and detergent qualities cannot be expected from a
soap if solubility is so low that the consumer must rub the soap between the
palms a great deal to yield sufficient lather.

No fats with crude or bad odors can be used for the manufacture of soap
base. This applies especially to animal fats of originally bad quality or not
sufficiently purified. Hardened fats are frequently objectionable because of
their hydrogenation odor, which tends to develop in the soap on standing.
The use of a few per cent of rosin has some advantages. It is able to cover
certain off-odors which may develop, and act as a preserver of the perfume
composition and as an inhibitor against rancidity.

Chapter XXXI discusses rancidity and its prevention in soap. It should
only be mentioned here that toilet soap base containing large proportions
of unsaturated fats such as greases, peanut oil, etc. tends more toward ran-
cidity than other charges. Certain catalysts promote the tendency for dis-
coloration and autoxidation, particularly metals such as copper in traces and
certain aromatic chemicals. Palm oil bleached with air may contain very
large amounts of fatty peroxides. Coconut oil fatty acids kept for a long
time in iron drums always contain large amounts of iron.

The following are general conclusions which can be derived from the the-
oretical knowledge of properties of fats and their soaps. With increasing
molecular weight the solubility of the sodium soaps decreases. In the same
sequence, the lathering qualities increase till lauric acid is reached in the
series; from here downward the lathering capacity is gradually lost. In the
sequence of increasing molecular weight, the bubbles of the suds become
smaller in size, but the foam becomes more stable. At the same time, de-
tergency decreases, electrolyte stability diminishes, and the toxic action on
the human skin decreases.

The hardness of the soap depends on the iodine value of the fats and
on the molecular weight of the fatty acid: the lower the iodine value and
the higher the molecular weight, the harder the soap will be. A high molecu-
lar weight involves a low saponification value. In order to produce a hard
soap, a fat charge with low iodine value and low saponification value
should be selected. Coconut and palm kernel oils have high saponification
values, but owing to their extremely low iodine value they still produce hard,
even brittle, soaps. Rosin is an exception, since it has a low saponification
value and yet produces a soft soap.

Solubility and lathering property are generally higher in soaps from oils
with higher iodine values and high saponification values. Again, coconut
oil has an extremely low iodine value, but a very high saponification value,
so it furnishes a special kind (palm kernel oil, babassu oil, and the like are
similar) of hard soap which dissolves easily and lathers well in cold water.

(b) *The I.N.S. and S.R. Factors of Webb.* Webb[4a] proposes a practical

formula for the estimation of the properties of a soap based on the chemical characteristics of the fat charge or of those of the particular fats used. He derives his formula from the same considerations described above. He proposes the *I.N.S. factor*, which is the saponification value minus the iodine value. It is obvious from the above that the higher the I.N.S. factor, the harder will be the soap of the particular fat. Table XVIII-7 contains I.N.S. factors for several fats.

For the proper estimation or prediction of the properties of a given concentration, Webb[13] proposes the *soap solubility ratio* (S.R.), which, for a fat charge, is calculated by dividing the I.N.S. factor of the mixture by the sum of the I.N.S. factors of the oils present in the mixture possessing a factor higher than 130 (including palm kernel and coconut oils).

TABLE XVIII-7

I.N.S. FACTORS FOR SEVERAL FATS[4a]

Coconut oil	250	Lard	137
Palm kernel oil	235	Olive oil	108
Vegetable tallow	165	Peanut oil	102
Mutton tallow	155	Cottonseed oil	85
Beef tallow	150	Corn oil	79
Palm oil	146	Soybean oil	54
Bone grease	143	Linseed oil	15

A fat charge mixture for t oilet soap base should have an I.N.S. factor of 160–170 and an S.R. ratio between 1.3 and 1.5, but not higher than 1.7. For household soaps of the types produced by fitting and settling on niger, the I.N.S. factor might be lower, ranging between 120 and 160, and the S.R. between the limits 1.5 and 1.9.

Lederer[14] calculated for some practical examples of fat charges the respective I.N.S. and S.R. factors. He found that, while the I.N.S. factor, to a certain extent, offers a proper indication, the S.R. factor, in many cases, fails to give a true picture of the properties of the soap.

Apart from this, it must not be forgotten that the hardness of soap and, to a certain degree, its foam properties, are very much dependent on the boiling method used. It has been shown, for instance, that it is possible to produce hard soaps from peanut and cottonseed oils when the curd is boiled for a long time on concentrated lyes. It should be noted that the foaming properties of such soaps can also be influenced by the boiling method. It has been found that soaps prepared by the process of boiling clear on concentrated lyes display a peculiar property of producing a "sticky," slimy, layer, when

[13] E. T. Webb, *Chem. Trade J.*, 77 (1925), 59.
[14] E. L. Lederer, *loc. cit.*, p. 17.

used with water, which is never found in other soaps. Such soaps also have somewhat better lathering qualities than ordinary curd soaps produced from soft oils.

(c) *Rayner's Experiments*. The practical approach of Rayner[15] to the problem of "pan charge and physical properties" should be reported here. We cite from his experiments, in which the properties of soap are measured by three mechanically standardized methods:

(a) *Determination of hardness*. The test machine measures the resistance in pounds which a bar of soap moving at a standard rate offers to a cutting wire attached to a spring balance. . . The apparatus was found to be sufficiently accurate for . . . recording hardness figures of 20 lbs. to 1.25 lbs over the range of samples examined.

(b) *Determination of solubility*. This was made by determining the time in minutes required to dissolve completely a 0.25 in. cube of soap fixed in a copper gauze box attached to a rotating frame immersed in water at the required temperature. By suitable illumination of the box, it was found possible to observe the point of complete solution.

(c) *Determination of rate of abrasion*. This apparatus was designed to measure the relative wastefulness of the soaps in practical use. A piece of the soap to be tested is carefully cut to the size of 2 in. by 2.5 in. by 3.75 in. thick, and this is fixed to a base plate in a copper bath containing the water and friction gear. The friction gear consists of a heavy metal plate of the same dimensions as the piece of soap, covered with a layer of flannel and during the period of the test the friction gear causes the plate to move backward and forward at a uniform speed and pressure, the soap being thus submitted to a regular amount of friction.

After the required treatment has been given, the water is emptied from the bath, and the soap is removed, freed from surplus moisture and weighed. The loss in weight thus measures the amount of soap which has been rubbed or dissolved away from the surface, together with such a relatively small amount as has been dissolved from the edges and underneath the surface which is pressed close to the base.

The loss of weight in grams is recorded as the *abrasion number*. In the case of determinations carried out at 60°F., a suitable time for the test was found to be 20 minutes; and in the case of hot water—100–110°F., 10 minutes. . . .

The comparison of properties was carried out after a series of oils and fats had been saponified and fitted to a similar degree of fineness, and contained 0.1–0.3% of salt and 0.1% free alkali. Rayner's results are given in Table XVIII-8. There are a number of interesting conclusions to be drawn from these figures. (1) The hardness of sulfur olive oil soap is not lower than that of tallow soap. Palm oil soap is twice as hard as tallow soap, although both have almost identical titers. Coconut and palm kernel oils furnish the hardest soaps. (2) Tallow, palm oil, and highly hardened whale oil produce the least soluble soaps, while coconut oil, palm kernel oil, sulfur olive oil, and soybean oil produce the most soluble soaps, and peanut, cottonseed, and slightly hardened whale oils occupy a middle position. (3) The most wasteful soaps are those made, peanut oil, and soybean oil soaps, which

[15] A. Rayner, *Soap, Perfumery and Cosmetics*, *11*, 1086–1088 (1938); *12*, 49–51, 152–153, 324–326, 345 (1939).

TABLE XVIII-8

PHYSICAL PROPERTIES OF INDIVIDUAL SOAPS[15]

Kind of soap	% FA	Titer, °C.	Hardness ratio, lb.	Solubility, min.		Abrasion No., g.[b]			Solubility No.[a]	
				100° F.	110° F.	60° F.	100° F.	110° F.	100° F.	110° F.
Coconut	59.3	23.4	20	10	8	3	45	54	100	125
Palm kernel	59.5	23.0	15	10	9	4	47	57	100	111
Tallow 1	60.1	43.9	3	195	65	7	7	12	5.1	15.3
Tallow 2	60.9	44.0	2.75	—	—	—	—	—	—	—
Sulfur olive oil[c] 1	60.5	16.0	3	8	6	14	M	M	—	—
Sulfur olive oil[c] 2	58.5	28.0	2.75	—	—	—	—	—	—	—
Sulfur olive oil[c] 3	60.3	17.5	2.5	—	—	—	—	—	—	—
Palm oil	60.9	45.0	5	190	60	4	6	10	5.3	16.6
Skin grease	60.3	40.0	2.5	—	—	—	—	—	—	—
Peanut oil	60.0	23.0	1.25	21	14	12	M	M	—	—
Cotton oil	60.6	34.6	1.75	18	13	9	20	M	55	77
Hardened whale oil 1	61.7	31.0	2	23	19	9	16	20	43	52
Hardened whale oil 2	63.1	44.0	7	270	90	1	5	9	33.1	11.1
Soybean oil	61.2	20.0	1.25	9	7	23	M	M	—	—
Olein	60.8	10.0	2.5	—	—	—	—	—	—	—

[a] 1000 divided by the time of solution of the standard in minutes.

[b] M, melted.

[c] Extracted oil from olive oil press residues.

melt at 100°F. in the abrasion machine. Cottonseed oil soap melted only at 110°F., and was, curiously, less wasteful at 100°F. than coconut oil soap. Coconut oil soap was less wasteful in the cold than tallow soap, but greatly exceeded tallow soap in the hot state. A very important property of tallow and palm oil soap is that their abrasion number (or wastefulness) does not change very much in moderately warm water.

Table XVIII-9 shows the determinations made with various fats.[15] The conclusions from these experiments are as follows. (1) The properties of soaps from an individual fat are not appreciably changed when mixed with other fats, and the properties of the mixture can be predicted from the nature of the composition. "(2) The higher the content of coconut oil or palm kernel oil, the harder will be the soap, and this will influence its hardness far more than the content of solid fats such as tallow and palm oil. (3) Provided there is not a wide difference in solubility, the harder the soap is, the less waseful will it be in cold water; and high solubility in cold water will be

TABLE XVIII-9[15]

| No. | Fat composition, parts | % FA | % titer | Hardness ratio, lb. | Solubility No., min. 110°F. | Abrasion No., g. | | factor | SR I.N.S. |
						60°F.	110°F.		
1	Grease 85, Coconut oil 15	62.6	36.2	3	33	7.0	19	140	1.08
2	Tallow oil 70, Coconut oil 30	61.4	29.7	2.75	77	13.5	30	157	1.48
3	Tallow 75, Coconut oil 25	61.8	37.4	2.75	38	11.0	25	161	1.44
4	Tallow 50, Coconut oil 50	61.9	33.1	4.5	77	8.0	30	179	2.36

caused more by the presence of soaps of liquid fatty acids rather than by those of the coconut oil group. (4) Wastefulness in hot water, on the other hand, unless the solubility is practically identical, will be governed almost entirely by solubility, which with commonly occurring mixtures varies over a range sufficient to vitiate any difference in hardness."[15] (5) In comparing the *de facto* determined solubility of the four soaps with the solubility ratio factor of Webb, it is obvious "that no general reliability can be placed on this factor, since No. 2 and No. 4, while having an actual observed solubility which is identical, have widely differing solubility ratios."[15]

In a further series of determinations, milled toilet soaps of good quality have been compared with the properties of 63% laundry soaps.

These last investigations show the surprising result that toilet soaps, in spite of their carefully compounded fat charges, their higher fatty acid concentration, and their apparent higher hardness, are relatively more wasteful than good laundry soaps containing only 63–65% of fatty acids. The reason

can only be found in the specific physical state into which the toilet soap had
been transformed through the milling procedure. In this connection we must
remind the reader that, depending upon the conditions in which the soap mass
had been worked during milling, the soap may appear in a number of crys-
talline forms. When dealing with this matter, it was explained that the prop-
erties which undergo changes with the varying crystalline forms are solubility
(abrasiveness) and foaming power (Chapter III, Section 4).

(B) ROLE OF COCONUT OIL IN THE FAT CHARGE

It could be seen from Rayner's experiments that coconut oil has a low
abrasive factor at 60°C., which, however, increases with rising temperature.
This means that, in soaps which are mainly used in cold solutions, a large

TABLE XVIII-10

PHYSICAL PROPERTIES OF TOILET SOAPS AS COMPARED WITH LAUNDRY SOAPS[15]

Sample	FA, %	Titer, °C.	Mean mol. wt.	Hardness, lb.	Solubility No., 110°F.	Abrasion No. 60°F. 20 min.	Abrasion No. 110°F. 10 min.
A	82.5	34.1	262	$4\frac{1}{2}$	80	27	34
B	81.5	36.9	272	$5\frac{1}{2}$	83	32	37
C	81.0	37.5	262	$7\frac{1}{2}$	81	15	29
D	80.9	37.1	263	5	80	23	32
LAUNDRY SOAPS							
A	65.3	28.8	263	$3\frac{1}{2}$	133	11	40
B	65.7	31.7	267	$3\frac{1}{4}$	125	16	44
C	64.6	31.3	269	$3\frac{1}{4}$	111	17	39
D	63.2	20.0	240	$3\frac{1}{4}$	170	33	81

proportion of coconut oil did not make itself felt as particularly wasteful.
But in bath soaps, for instance, this would be detrimental for the lasting prop-
erties of the soap.

Some workers, who limit the proportion of coconut oil in the fat charge of
toilet base to a maximum of 10%, maintain that a higher proportion of coco-
nut oil would cause the base to retain quantities of salt that exceed the al-
lowable standard and that such a soap could not be milled to a satisfactory
product. Others are of the opinion that the minimum should be 15%, but
that good toilet bases can be boiled with 30% of coconut oil in the fat charge.
However, this last figure is undoubtedly an overestimation of how much coco-
nut oil a properly composed toilet soap should contain. Such a base would
become quite brittle, especially after drying to the required 80% fatty acids.
Even the lather would not be of the required quality; although voluminous,
it is thin and easily collapsed.

Therefore, probably the best practice is to include in the fat charge not less than 15%, but not more than 20%, of coconut oil or palm kernel oil. Whether to use the minimum or the maximum limit will depend on the rest of the fat charge. In the presence of soft oils like peanut oil or even lard, it is possible to use the lower limit.

(C) Fat Charges for Toilet Soap Bases

(1) 85 parts tallow (first quality)
     15 parts coconut oil (first quality)
(2) 75 parts tallow (first quality)
     10 parts peanut oil (light quality)
     15 parts coconut oil (first quality)
(3) 50 parts tallow (first quality)
     38 parts lard
     12 parts coconut oil (first quality)
(4) 40 parts palm oil (bleached)
     45 parts tallow (first quality)
     15 parts coconut oil (first quality)
(5) 55 parts palm oil (bleached)
     20 parts olive oil
      7 parts castor oil
     18 parts coconut oil

(D) Boiling of Toilet Soap Bases (Saponification, Washes, and Fitting)

Boiling of soaps of the purity required for toilet soap base must be carried out by the indirect method.

First day's operation. The fat charge, with the exception of the coconut oil, is pumped into the kettle and boiled through with direct steam until the charge is melted down. Some 10% of the total caustic alkali needed is now brought into the kettle in the form of 15–20° Bé lye. The steam valve should not be opened wide at this stage, and the kettle should only boil gently. After the first batch of lye is absorbed and the pan content has become closed, a new portion of the caustic may be introduced and boiling continued until the mass appears well emulsified, a new addition of caustic made, and so on, until the soap retains considerable lye strength. After the last batch of caustic has been added, the test with chemical indicators should show a strong color. If a separation of the layer occurs during the saponification period, no further lye addition should be made, and the pan should be boiled for a while until the excess alkali is used up, and only the proper excess remains that enables the pan to boil normally. It may become necessary to add some water in order again to bring the soap to the proper closed state. In general, the same principles govern the saponification process in this case as were described for the procedure with other soaps.

However, it must be remembered that, at the first stage of saponification, in the boiling of toilet soap base, only fats very sensitive to electrolytes are in the kettle, and this calls for great caution while the addition of caustic soda is being made.

When completely neutral tallow is used, it may happen that no emulsion is formed at all at the beginning of the saponification. In such a case the best thing to do is to shut the steam for a period of 1 to 2 hours to give the mass a chance to start saponification. When this takes place, the mass produces considerable heat and rises in the kettle. Such a practice is not without its dangers, since sometimes the saponification reaction may set in with such violence that the pan content suddenly boils over. To prevent this, it is good practice to add some weak salt solution of about 6° Bé to the kettle. The practical soapmaker's methods for judging the state of boil by tests were described earlier in this chapter and these tests also may be applied in this case.

Toward the end of the saponification process, acid soaps in the soap mass may be produced with all that this implies (excessive viscosity, bunching, etc.). This happens through lack of sufficient quantities of electrolytes in the kettle, and can be prevented by adding about 1%—calculated on the fat charge—of 20° Bé salt solution to the pan contents, at the point when most of the total calculated caustic lye has been used up. The soap solution will become much thinner at once, and the danger of bunching will be avoided.

If, however, the mishap occurs and the soap becomes viscous, the only way out is to add, at once, a large portion of lye and to boil vigorously until the soap has thinned out again. The earlier the inclination of the soap for bunching is detected, and the sooner the countermeasures are taken, the easier it will be to repair the damage already done.

When the soap, at the end of the saponification period, is found to be sufficiently homogeneous, and all the tests described earlier are satisfactory, the next operation (salting-out) may start as usual. With this type of soap it is important that the soap have a high degree of mobility before graining is carried out. Sufficient water should be added until the pan boils in an easy manner and the soap solution also glides from the trowel with a certain fluidity.

When a large excess of alkali must be disposed of, it is done by adding some coconut oil and boiling the mixture. Coconut oil combines very readily with the excess caustic soda under these circumstances.

Only pure salt should be used for the salting-out operation. The finely granulated salt is spread over the whole surface of the kettle while the contents are kept steadily boiling during the whole period. One must be sure that salt is never dumped in lumps. and in excess, into the kettle. The mass should be tested at frequent intervals with the trowel and, as soon as separa-

tion into curd and lye is indicated, the addition of further salt must be stopped. Boiling is now continued for about an hour in order to rid the curd of the adsorbed salt.

A good toilet soap base should never contain more than a certain minimum of salt. This is why salting-out should never be done on lyes stronger than 10–12° Bé. More concentrated lye requires the use of quantities of salt over and above the normal. The appearance of a properly grained, but not oversalted, curd on the trowel and its aspect in the kettle are described earlier in this chapter. The methods for regulating water and electrolyte content accurately and for conducting the graining process according to a kettle plan are described in Chapter XVII.

The kettle is now covered and left to settle overnight.

Second day's operation. Next morning the lye is drawn off. As a rule, this is done by draining through the valve in the bottom of the pan by the natural head of the liquid; in some plants, the lye is pumped directly into the glycerine department. However, it is better practice to give the lye a chance to cool and precipitate the hydroxy fatty acid soaps or any other traces of soaps if still present.

The curd is still hot in the pan and in this state some 4° Bé caustic soda is added in an amount equal to about 8% of the fat charge. The caustic must be boiled through until the whole mass boils homogeneously. At this point, 38° Bé caustic lye is added in an amount equivalent to the coconut oil which will have to be introduced in the pan. Thereafter, the whole amount of coconut oil is added. In fact, a small excess of caustic beyond that required for the saponification of the coconut oil must be present. In these circumstances, there is sufficient electrolyte in the kettle and the coconut oil saponifies quickly and the mass boils easily and in the proper state of emulsion. The second graining is carried out by observing the same principles as described on the first day's operation. It is of utmost importance that no more salt should be used than is absolutely necessary. It is, in this case, not necessary to carry out the boiling clear operation.

Whether or not a third wash for glycerine recovery is made depends on the kettle plan to be followed.

Third day's operation—fitting. There is again a hot curd in the kettle. The procedure of fitting by the indirect method, which means by adding sufficient amounts of water or diluted salt and caustic solution to the curd until the proper amounts of niger and neat soap have been formed, is described in Chapter XVII and on p. 358 ff. In this case, caustic lyes or salt solution of 1–2° Bé is used for fitting.

The operator must decide on the type of fit desired for each type of soap, and the salt concentration must be adjusted accordingly.

The rational method, as described by Wigner, and the use of the mano-

metric gage for all processing of toilet soap base is recommended especially for beginners, although all practical tests of the empirical soapmaker have also been described in this chapter.

Everything that has been explained concerning neat soap yields and conditions for niger formation is also valid for the process of settling neat soap on niger for toilet soap base.

The purification and utilization of niger has been dealt with on page 360 ff. It must be borne in mind that thorough purification of the niger has special importance in the case of toilet soap base, since in this process everything must be avoided that would adversely influence the purity of the product.

FULL–BOILED UNSETTLED SOAPS

(1) Half-Neat, Eschweger, or Mottled Soaps

These soaps are well-known all over the European Continent and are held in very high esteem, particularly in Russia. The Germans used to be highly specialized in the manufacture of this kind of soap, for which, in the past, they had acquired command over the South American and West Indian markets. On the following pages, the method of boiling Eschweger soap in Germany is described in detail.

Eschweger soap is in itself a special class of soap with a characteristic "feather" or design, and this is the reason that, in some countries, it is called "unsettled soap." In a strict sense, this soap should be classed as a solid unsettled soap, since in its manufacture neither clear lye nor niger is drawn off. Nevertheless, it is also true that with this kind of soap the occurrence of niger or lye is involved. The difference from other processes, however, lies in the fact that in this case the layers never really separate into two distinct phases. Neat soap and niger remain intermixed, and this is the cause for the formation of the characteristic "mottle." The effect is obtained by the use of electrolytes (sodium carbonate, salt, sodium silicate, etc.) in such amounts as to cause an incomplete separation between the two phases which becomes visible after solidification in the forms. The finished Eschweger soap is a mixture of neat soap and niger. This is the reason for the classification of the soap as a "half-neat soap."

The popularity of Eschweger soap in the various parts of the world may be explained by its showy appearance, its content of useful ultramarine blue which may be considered by the customer to act as wash blue, its cheapness in comparison to neat soaps, and its ready solubility and good lathering prop-

erty. Of course, it is more wasteful in use than ordinary neat soaps, but it is said to be more economical when compared with unsettled soaps of other kinds.

The mottle is generally colored blue, but sometimes it is red, grey, or greyish blue.

The soap yield is generally between 205 and 210%. This applies only when, in addition to the electrolytes necessary for the partial separation of the layers, no other filling materials are added.

(A) FAT CHARGE

(1) 60 palm kernel oil
    20 lard
    20 tallow
(2) 40 palm kernel oil
    30 palm oil
    30 bone grease
(3) 40 coconut oil
    20 hardened fat
    20 cotton oil, neutralized
    20 lard

(4) 40 coconut oil
    20 tallow
    20 palm oil, bleached
    20 corn oil
(5) 40 coconut oil
    40 tallow
    20 peanut oil
(6) 55 palm kernel oil
    7.5 tallow
    22.5 bone grease
    15 cotton oil, neutralized

General rules for the composition of fat charges are:

(a) Not less than 35% of coconut or palm kernel oil should be used in the fat charge. (However, there are experts who maintain that even 15% of these oils would be sufficient, and in times of scarcity the use of less coconut oil may be attempted. The mottle may then not develop as perfectly.)

(b) The titer (solidification point of the fatty acid in the charge) should not be below 30°C.

(c) The saponification value of the fatty acids (neutralization value) should not be below 222.

The minimum batch for the manufacture of Eschweger soaps should not be below 1000 kg. With smaller batches there is danger of the soap cooling and solidifying before proper separation takes place, so that the required design will not be obtained.

There are two methods for the manufacture of Eschweger soaps. One procedure is similar to that described for the finishing of neat soaps settled on niger, so it is possible to produce the proper degree of separation by adding a certain amount of electrolytes to a homogeneous soap solution. This procedure is called the *direct method* (in accordance with the explanations given for the finishing of neat soaps). The *indirect method* is the procedure by which a neat or curd soap is diluted until it produces the required degree of separation.

(B) THE DIRECT METHOD

(a) Saponification. First, the cuttings are charged from the previous boil into the kettle. About one-third of the total caustic lye required as per

calculation is then added and boiling with open steam is carried on until the cuttings begin to dissolve. If the fat charge is composed of fatty acids instead of neutral oils and the saponification is carried out with the carbonate method, it is more difficult to dissolve the cuttings. In such cases it is advisable to collect the cuttings from a number of boils, and to produce Eschweger soap from them in a separate batch in the same manner but with caustic soda used as saponifying agent.

After the pan contents are well liquefied, the fat charge should be brought into the kettle and boiled until a test shows that almost no caustic remains. The saponification should now be completed as already explained. At the end of the saponification, 0.2% free caustic soda should be left in the soap.

(*b*) *Concentration*. The homogeneous soap solution, at the end of the saponification period, is generally too diluted for any further treatment. If this is the case, the solution must be concentrated and this is done by boiling by means of a closed steam coil. By boiling the pan contents, it gradually becomes clear and bright, the foam rises, the surface becomes smooth under the foam layer, and the foam layer gradually disappears. Concentration by this process should be carried on until the soap becomes so viscous that the steam evolved by evaporation within the mass breaks through by forming designs of white concentric rings on the surface. This design was called the *rose design* by the German soapmaker (the soap breaks through in roses). The appearance of this design discloses that the concentration of the soap solution has reached the proper degree for the following operation.

(*c*) *Liquoring*. The electrolytes used are salt, sodium carbonate, potassium carbonate, and sodium silicate. The first three are employed in powder or in solution form, while sodium silicate is always used in one of the solutions commercially available. In Germany, the 36–38° Bé was in use, while in the United States, mainly the 42° Bé form is used. It should be borne in mind that the latter grade is more alkaline than the former one, containing about 2 parts of SiO_2 to every part of Na_2O (see Chapter IX, Section 4).

Because salt has the strongest electrolytic action among all the electrolytes mentioned, its addition must be in small portions and with utmost care. If the caustic soda used during the saponification period contained any electrolytes, such as sodium carbonate, in larger proportions, as was the case in Russia in earlier periods, then further additions of electrolytes after the concentration process has taken place may become unnecessary. The electrolytes present may already be sufficient for producing the required separation.

Among all other electrolytes, probably the safest agent for this process is potassium carbonate. It is better than salt because of its slower and weaker separating or graining action, and by using it instead of salt there is less danger of oversalting or overdoing the separation into two layers. In comparison with sodium silicate, it has the advantage of keeping the soap plastic,

and not hard and brittle. Contrary to what happens when sodium carbonate is used, the soap never effloresces, that is, a white precipitation of sodium carbonate never appears on the soap surface.

The following is a practical test for the determination of the degree of separation.

A small sample about 1.5 inches in diameter is dropped on a glass plate and kept for 5 minutes in the vicinity of the kettle. It is essential that the sample should solidify, but not cool down too quickly. Therefore, in the summertime, it should be kept at some distance from the kettle. After 5 minutes, the sample should be solid, but it should be possible to squeeze out a drop of clear liquid soap when gently pressed with one finger.

Should the test turn out to be negative electrolytes must be added, in very small portions (particular care must be exercised when salt is used as electrolyte), and after each addition the glass test must be repeated. Utmost care is required at this stage in view of the danger of the charge becoming oversalted to such an extent that no correction is possible. In such a case the soap must be completely salted-out and the whole procedure started from the beginning.

Oversalting is indicated when, while making the glass test, a drop can be squeezed out even after a period of 7 or 10 minutes. Moderate oversalting can be corrected by diluting the salt concentration by addition of soap. This can be done by pumping some additional fat charge into the pan, saponifying, and finishing as above. The main condition to be fulfilled is to maintain the proper soap concentration. With the proper concentration the quantity of electrolytes present is sufficient to effect the desired degree of separation.

If the electrolyte concentration has been pushed so far that the pan contents display a too diluted appearance, boiling without the typical rose formation, the boil is beyond correction. An oversalted condition can also be detected by the *flutter* test. When the soap flutters in large bubbles when thrown from a trowel, separation has been pushed too far, and the kettle space would be insufficient for an attempt to dilute the salt concentration by addition of soap made from fats added on top of the soap already in the kettle.

(*d*) *Dyeing*. After the proper conditions (free caustic, water, and electrolyte contents) have been adjusted and regulated, the dyeing of the soap should be carried out. Ultramarine blue, iron oxide, or red clay is used as coloring matter. 2 kg. of ultramarine blue, 2–3 kg. of red clay, or 1 kg. of iron oxide is used for 1000 kg. of fat charge. The colors are prepared by mixing with boiling water in a proportion of 3 : 1 color to water, along with a small addition of caustic soda. The color suspension is added to the soap while still boiling; the steam must be shut off immediately hereafter.

(*e*) *Cooling in Frames*. The colored soap must be filled in forms of suitable size. The frames should not be too small, since congealing would set in after too short a period and there would not be sufficient time for the soap to produce the proper separation and design. On the other hand, too large a

frame would keep the soap liquid for a long time, entailing the danger of too extensive separation, and resulting in the color settling down and the design developing in the lower part of the soap slab only. When steel frames are used for molding, it is advisable to cover the frames well against too quick cooling of the walls. Some soapmakers prefer to agitate the contents of the frames until it is cooled down to a suitably low temperature.

(C) Defects and Troubles

(1) The consequences of a deficiency or an excess of electrolyte and the means for detecting, preventing, and correcting them have been explained.

(2) Deficiency or excess of water always manifests itself by a thin consistency of the boil. With too little water the electrolyte concentration thins out the pan contents, and with too much water the soap becomes excessively liquid simply because of the dilution. Whether the reason for the trouble was too much or too little water in the pan can be discovered easily by boiling on and observing the kettle condition. When the boil regulates itself and becomes normally viscous again, this indicates that there was too much water in the kettle (it simply evaporated by continued boiling). But when there is sufficient water in the kettle, the consistency of the soap becomes even more liquid by boiling—because with further evaporation of water the electrolyte concentration and, consequently, the cause for its liquidity, increases.

(3) *Splashed mottle.* Eschweger soap is said to have a splashed mottle when the coloring matter is divided too finely over the body of the soap. This is a consequence of too concentrated soap, but it may also be caused by the use of too much tallow or similar fats in the fat charge.

(4) Too much free alkali in the soap prior to the saponification with electrolytes produces the same effects as an excess of electrolytes.

(D) Composition of Normal Eschweger Soap in Various Stages of Production

Fat charge: 2000 kg. 55 parts palm kernel oil, 22.5 parts bone grease, 7.5 parts tallow, and 15 parts cottonseed oil.

The saponification value of the charge is 221. For saponification of 100 kg., 15.76 kg. of NaOH is needed. For regulation of the alkalinity at the end, another 0.4%, (16.16 kg.), and for 2000 kg. of fat 323.2 kg. of NaOH are necessary. Technically, the caustic soda contains only 94.1% NaOH; consequently, 343.5 kg. of commercial caustic soda is used. The calculated amount of caustic soda is dissolved in 1800–1900 kg. of water, and the fat charge is saponified and strengthened as described above. The direct method is being used in this experiment. See Table XIX-1.[16]

[16] L. Ubbelohde and H. Heller, *Chemie und Technologie der Seifen und Waschmittel*, Hirzel, Leipzig, 1930, p. 478.

TABLE XIX-1

ANALYSIS OF MOTTLED (ESCHWEGER) SOAP IN THREE STAGES OF ITS PREPARATION[16]

Constituents	1st stage—soap before electrolyte addn., %	2nd stage—soap after electrolyte addn., %	3rd stage—soap ready in forms, %
Fatty acids	49.26	48.03	48.78
Na₂ combined	6.02	5.90	6.08
NaOH	0.19	0.18	0.18
NaCl	0.27	1.91	1.97
Na₂CO₂	Traces	Traces	Traces
Water	44.26	43.98	42.00

Eschweger soap was produced from the same fat charge; but instead of salt, sodium silicate was used as electrolyte. The results obtained are given in Table XIX-2.[16]

Examination of Eschweger soap boiled from a fat charge containing 60 parts of palm kernel oil, 30 parts of tallow, and 10 parts of lard gave the data shown in Table XIX-3.[16] Sodium silicate was used as electrolyte.

This last investigation reveals a number of facts. Separation of the layers is produced very similarly to the process taking place when neat soap separates from niger. Here, too, there are two phases, one phase containing more, and another less, fatty acids. The difference, however, between the fat concentration of the two layers is not very great. It should be noted that the practical salting-out of the different fatty acids and their distribution between the two layers are much more distinct in this case than with settled soap on niger.

(E) THE INDIRECT METHOD

This method is used when the fat charge contains impure ingredients, like certain kinds of tallow and bone grease.

TABLE XIX-2

ANALYSIS OF MOTTLED (ESCHWEGER) SOAP IN VARIOUS STAGES OF ITS PRODUCTION (SODIUM SILICATE USED AS ELECTROLYTE)[16]

Constituents	Soap before electrolyte addn., %	Soap after electrolyte addn., %	Soap in forms, %	Ready soap separated in	
				Curd, %	Feather, %
Fatty acids	47.36	44.95	46.53	50.84	42.45
Na₂O combined	5.94	5.68	5.78	6.32	5.39
Na₂O combined with SiO₂	—	0.90	0.93	0.08	1.07
NaOH	0.16	0.20	0.21	0.02	0.44
NaCl	0.27	0.24	0.26	0.02	0.29
Na₂CO₂	0.13	0.12	0.12	0.01	0.15
SiO₂	—	2.43	2.61	0.23	3.02

At the start, only the ingredients other than coconut and palm kernel oils are saponified, and graining is carried out with great care, lest the neat should should be oversalted, the excess salt causing difficulties afterward at the finishing operation. To make certain that no trouble of this kind occurs, it is a good practice at this stage to use caustic soda instead of salt for graining. In case of an overcharge it is easy to eliminate the excess NaOH by adding some coconut oil and neutralizing the caustic by saponification.

After the curd has formed, ample time for separation of the layers should be allowed, especially when salt is used as electrolyte. The spent lye should be well drained.

TABLE XIX-3

ANALYTICAL DATA ON MOTTLED (ESCHWEGER) SOAP FROM PALM KERNEL OIL, TALLOW, AND LARD[16]

Constituents	Soap before electrolyte addn., %	Soap after electrolyte addn., %	Soap in forms, %	Ready soap separated in	
				Curd, %	Feather, %
Fatty acids	29.26	48.03		52.48	44.3
Na_2O combined with fatty acids	6.15	5.84		6.28	5.41
Na_2O combined with SiO_2	—	1.03		0.22	1.38
NaOH	0.22	0.25		—	0.47
Na_2CO_3	1.52	1.36		—	1.54
SiO_2	—	3.81		0.84	4.98
Melting point of fatty acid	30.2	—		30.8	26.1
Iodine value	27	—		32.7	21.0
Saponification value	227	—		216.5	233

The cuttings from the previous boil and then the caustic lye necessary for the saponification of the coconut or palm kernel oils should be added to the curd in the pan. From now on, the Eschweger soap may be finished either by the direct method, as was described above, or by the indirect method. The pan contents are again carefully salted-out with caustic soda. After a very thorough separation of the layers, the curd receives sufficient water to be suitably adjusted for the following operation of final electrolyte treatment. Before these are added, the glass test should be made in order to ascertain whether or not sufficient electrolyte is already present in the kettle from the previous operations.

The addition of water can be made with greater assurance when it is carried out with the help of analytical control. For this purpose, the fatty acid contents of the soap curd must be ascertained, by the wax cake method Chap. XXXIX). If the curd contained 56% of fatty acid, according to previous experience the soap should contain 50% of fatty acid when finished and

separated with electrolytes. With 2500 kg. of curd in the kettle, this would correspond to $(2500 \times 56)/100 = 1400$ kg. of fatty acid. To dilute to a soap solution with 50% of fatty acid, add 300 kg. of water as $100 \times 1400/50 = 2800$, and $2800 - 2500 = 300$. The manometric gage could be used in such cases with great convenience.

In this connection, it should be understood that mottled soaps are sometimes made by mechanical means from full-boiled soaps. This is particularly true in America, where the production of mottled or Eschweger soap is very limited and would not warrant a change in the normal boiling procedure. One method used is to run the soap from two crutchers together into one frame. The soap in one of the crutchers is colored, so that a mottled effect is obtained by the mixing.

(2) Homogeneous Unsettled Soaps

These soaps remain homogeneous after the fat charge has been saponified, and are discharged from the kettle in this state directly as a finished product. No salting-out whatsoever takes place from the beginning to the end.

This should not mean that no electrolytes at all are used in this process. They are used, but only to a certain extent and in quantities insufficient to cause salting-out of the soap.

For the manufacture of these soaps, oils and fats are used mainly with high lye limit concentration, the soaps of which are not easily salted-out from their solutions. Such soaps are able to withstand very high electrolyte concentration, and their saponification can therefore be carried out easily, without any danger of disturbing the homogeneity of the soap solution. It is even possible to incorporate appreciable quantities of electrolyte solution in such soap solution, thus increasing the yield of the soap (see filling of soaps, Sect. 5). But even when no such intention exists, it must be borne in mind that the only oils and fats that may be successfully treated and saponified by concentrated caustic lyes belong to the class of the coconut oil types with high saponification numbers.

Oils and fats with low saponification values (tallow, peanut oil, and the like) cannot be saponified with concentrated lyes by the boiling process when not followed by salting-out and settling. Since the soaps of such oils are promptly salted-out in the heat, the reaction would not proceed at all. On the other hand, in order to saponify such oils it would be necessary to use lyes diluted to such an extent that, as a result, after solidification no solid soap, but a congealed mass only, would be obtained. It is therefore impossible to produce hard unsettled soaps from this sort of charge by the boiling process.

Mixtures of coconut oil and oils with low saponification value are, however, quite suitable for the manufacture of such soaps, and it is even possible

to introduce considerable amounts of electrolyte solution into the soaps without running any risk of its separating into phases. For the production of highly fitted soaps it is necessary to leave the electrolyte-susceptible fats out of the fat charge altogether. Soaps intended to be fitted to yield over 500% must be produced exclusively from coconut oil, since palm kernel oil soap has a far smaller capacity for taking up electrolytes than does coconut oil soap. When these soaps are produced from neutral oils, the product contains the whole amount of glycerine originally present in the fat charge.

When fatty acids are used in the fat charge, the problem of glycerine does not occur at all. They are also cheaper than neutral oils, since 95 parts of fatty acids would yield the same amount of soap as 100 parts of neutral oil, the glycerine residue amounting to about 5% in the neutral oil. Saponification can be achieved in this case with the cheaper sodium carbonate, instead of with the more expensive caustic soda. The presence of glycerine, its value as an ingredient in soap, and the advantages and disadvantages connected with this, have been discussed extensively. Glycerine is a plasticizer in soap and an emollient as a cosmetic ingredient. Soap when containing glycerine is able to withstand higher electrolyte concentrations than without it. Merklen found the L.L.C. of olein soap to be 10.25° Bé, but when the same soap contained glycerine the L.L.C. rose to 17° Bé. On the other hand, glycerine does make soap sensitive to atmospheric condition, and renders it hygroscopic.

There are a great variety of unsettled soaps all produced by some kind of saponification process and resulting directly, without any intermediate separating process, in a hard soap product. Let us consider here only three examples (see also Part D).

(a) *Shaving soap*. The fat charge contains stearic acid, coconut oil, and some other oil. The necessary amount of caustic potash and soda is charged in the kettle. Then coconut oil is added and partly saponified by heating and agitating. It is true that in most cases this is done with indirect steam, but there are factories where this first stage is carried out with the boiling process. In the second stage the stearic acid is saponified with the remaining alkali and the resulting hard product is treated as toilet soap.

(b) *Salt-water soaps*. The kettle is filled with the calculated quantities of 25–30° Bé caustic, and coconut oil is gradually added and saponified with open steam. Saponification takes place very quickly. The pure soap may be poured into forms as such, but generally it is filled with electrolyte. In fact, it would not be worth while to produce such soaps by the boiling process, as they can be produced with the cold process as well. It is mainly because of the filling of the soap and for the process of running that the soap mass is kept sufficiently hot, and it is for this purpose that the boiled process is used (see filling of soap, Sections 3 and 5 following).

(c) *Soaps produced by the carbonate saponification process*. Any fat

charge containing only fatty acid can be saponified and finished as a boiled, but unsettled soap. Whenever pure fatty acids are saponified, they may be just saponified by boiling through quickly with sodium carbonate, getting rid of the free carbon dioxide, and finishing by merely pouring the homogeneous soap solution into frames or cooling presses. This is probably the most modern development in soap manufacturing. Fatty acids can be produced in such pure form and to such selected standards that they can be used without any difficulty in the cheap and easy process as outlined here.

(3) The Manufacture of Soft Soaps

Soft soaps are mainly produced by the full-boiled process, but without any graining, once saponification has been completed.

The raw materials are liquid oils and mainly caustic potash. There are certain kinds of soft soaps which also contain some tallow, and in the production of others some caustic soda is used. Soft soaps, as a general rule, contain far more water than neat or curd soaps. They also contain certain electrolytes, mainly potassium carbonate and potassium chloride. An example of a soft soap which does not contain such additions is the U. S. P. soft soap for medical purposes, also called *Sapo Kalinus*.

Electrolyte additions are made during saponification by mixing the caustic potash with the necessary amount of carbonates. The soapmaker calls such mixed lyes *reduced lyes*. It is also customary to define the *causticity ratio* of lyes and to call a lye containing only a small relative amount of potassium carbonate a "strongly caustic lye," whereas when large quantities of carbonate are present, the lye is called "weakly caustic."

The pure potassium salt of the fatty acid would consist of a viscous, not completely transparent, mass. The proper commercial product is obtained only after the potassium carbonate solution has been added to the soft soap, as required. It should be transparent and present a soft, but not a tough gelatinized mass. Small amounts of added electrolytes reduce the viscosity of the solution. Increased amounts, of course, ultimately salt-out the pure soap from its solution.

Soft soaps are much more soluble in water than soda soaps. The increased solubility results from the use of caustic potash as saponifying agent. and the fact that these soaps always contain liquid fatty acids of unsaturated oils.

In Central Europe, this class of soft potash soaps was considered as one of the most important group of soap products, and huge quantities have been sold directly for household purposes. Such soaps were put to every possible use in the home: the poorer population used it for their house laundering, for washing dishes, and floors. Soft soaps were sold in very large quantities to factories for all kinds of industrial purposes and to ships for scrubbing the

decks, as well as for agricultural, horticultural, medicinal, and veterinary purposes.

In these European countries, the manufacture of soft soaps has developed to a degree of specialization which, as far as we know, has not yet been surpassed in any other part of the world. It is therefore, in our opinion, of value to describe the manufacture of this class of soap in some detail closely following European lines of production.

The following three main groups of soft soaps were manufactured in Europe: (1) smooth soft soaps, (2) soft soaps with grain (or "fig," see Section E following), (3) white soft soaps or silver soaps.

(A) SMOOTH SOFT SOAPS

For the manufacture of soft soaps, caustic potash of 50° Bé is generally used. The amounts necessary for the saponification of 100 kg. of oil can be obtained from Tables XII-4 and 6 by multiplying the saponification values given by the factor 0.196. The saponification value itself may be taken as the amount of pure KOH (in kg.) needed to saponify 1000 kg. of fat or oil.

However, it is possible that certain grades of commercial potassium hydroxide contain greater or smaller amounts of impurities than are customary and, in these cases, it becomes necessary to calculate the proper amount of commercial product from the practically required amount. Table XII-6 contains the corresponding data for the saponification of fatty acids. The figures given for KOH should be multiplied by the factor 1.96 to give the amount of KOH 50° Bé.

The "reduction" of the caustic potash lye with potassium carbonate or other electrolytes should be made with due consideration to the temperature of the season. An electrolyte addition makes the soap softer and, at the same time, the temperature sensitivity of the soap becomes greater. It is therefore obvious that less "reduction" should be made in the summer and more in the winter. The question of consistency is one of the biggest problems with these soft soaps, especially in connection with the variation of the seasonal temperatures. Consistency should remain uniform throughout all seasons. To satisfy this requirement, it is necessary, in summer, to replace some caustic potash by caustic soda. Soft soap remains smooth in summer, even when the fat charge contains more saturated fats, like tallow or any other fats containing saturated acids. Soft soaps produced of such fat charge might become too hard in winter, or produce hard, crystalline granules (fig) and, in such cases, lose their transparency.

(a) *Lyes and Their Reduction.* The following are some samples for lyes reduced to various degrees, in order to be suitable for the different seasons of the year. (a) *Winter:* to 100 kg. of caustic potash 50° Bé add 3 kg. of calcined soda ash and 14 kg. of potassium carbonate or potassium chloride.

(*b*) *Summer:* to 100 kg. of caustic potash 50° Bé add 10 kg. of calcined soda ash and 12 kg. of potassium carbonate or potassium chloride. (*c*) *Winter:* to 100 kg. of caustic potash 50° Bé add 5 kg. of calcined soda and 10 kg. of potassium chloride. (*d*) *Summer:* to 100 kg. of caustic potash 50° Bé add 10 kg. of calcined soda ash and 3 kg. of potassium chloride.

The reduced lye is brought to the required strength by addition of water. When boiling is carried out with closed steam coils, the lye employed should be 35° Bé. When boiling with direct fire, which now is rarely done, the lye should not be more concentrated than 20–25° Bé. When boiling with open steam, the water added to the pan by condensation should be taken into consideration.

Some soapmakers do not prepare the reduced lye before the boil starts, but prefer to put the necessary amount of electrolytes separately into the kettle. In such cases the necessary amount of electrolyte is taken in relation to the amount of fat charge saponified. An example of this follows.

100 kg. of fat charge requires 7–10 kg. of potassium carbonate or 4–5 kg. of potassium chloride; the electrolytes are added in form of a 30° Bé solution.

Some good arguments may be brought forward in favor of this method, as in this case there is no need for preparing the mixture of electrolyte and caustic lye in a special container. The addition of the electrolyte solution should not be started before a certain part of the caustic potash has already been consumed by the fat charge. Only after at least one-third of the fat charge has been saponified in the kettle should the electrolyte solution be added and then gradually in between small portions of the caustic potash.

It is important to consider the difference between the properties of soft soaps produced with potassium carbonate and those produced by potassium chloride. Indeed, there are cases in which it is not advisable to use potassium chloride at all.

Potassium carbonate is hygroscopic; the chloride is not. The carbonate consequently serves not only as a consistency regulator, but also as a humectant, like glycerine in cosmetic preparations. It is therefore more advisable to use potassium carbonate in a dry climate where there is a danger of the soft soap drying out. In a damp climate, potassium chloride may safely be used.

There is another danger connected with the drying out of soaps conditioned by potassium chloride. As a consequence of drying out, the soap becomes concentrated with respect to potassium chloride and this may go as far as to induce some graining whereby a small quantity of lye separates. It is important to note in this connection that the relative graining efficiency of potassium chloride is higher than that of potassium carbonate. Such condi-

tions may sometimes be observed with soft soaps in their containers when the soap, instead of sticking to the walls of the container, shows a tendency to slide.

The following oils can be used in fat charges for smooth soft soaps: linseed, soybean, and fish oils in winter; in the summer season, these oils, or their fatty acids, may be replaced by oils and fats containing higher proportions of stearic acid, like sunflower, peanut, cottonseed, and other oils. Rosin and tall oil may be used both in the summer and in the winter.

In the following section some fat charges are proposed which would produce the required consistency and appearance when saponified with the proper amount and kind of lye. The lye suggested for this purpose may be prepared in the following way: to 100 kg. of caustic potash of 50° Bé, 15 kg. of potassium carbonate is added and the mixture diluted with water to a concentration of 25° Bé.

FAT CHARGES

For autumn and spring:

(1) 400 kg. linseed oil
   70 kg. water (approx.)
   400 kg. caustic potash 25° Bé reduced
   95 kg. caustic soda 25° Bé (approx.)

(2) 400 kg. soybean oil
   70 kg. water (approx.)
   405 kg. KOH 25° Bé red.
   90 kg. NaOH 25° Bé (approx.)

(3) 180 kg. linseed oil
   180 kg. peanut oil
   40 kg. rosin
   70 kg. water (approx.)
   400 kg. KOH 25° Bé red.
   85 kg. NaOH 25° Bé (approx.)

(4) 150 kg. soybean oil
   150 kg. sesame oil
   50 kg. linseed oil
   50 kg. rosin
   70 kg. water (approx.)
   400 kg. KOH 25° Bé red.
   85 kg. NaOH 25° Bé (approx.)

For summer:

(1) 400 kg. linseed oil
   70 kg. water (approx.)
   350 kg. KOH 25° Bé red.
   135 kg. NaOH 25° Bé (approx.)

(2) 425 kg. soybean oil
   70 kg. water (approx.)
   385 kg. KOH 25° Bé red.
   125 kg. NaOH 25° Bé (approx.)

(3) 120 kg. linseed oil
   260 kg. peanut or cotton oil
   60 kg. rosin
   70 kg. water (approx.)
   380 kg. KOH 25° Bé red.
   125 kg. NaOH 25° Bé (approx.)

(4) 385 kg. soybean, maize or sunflower
    oils
   60 kg. rosin
   70 kg. water (approx.)
   385 kg. KOH 25° Bé red.
   120 kg. NaOH 25° Bé (approx.)

For winter:

(1) 426 kg. linseed oil
   63 kg. water (approx.)
   468 kg. KOH 25° Bé red.
   46 kg. NaOH 25° Bé (approx.)

(2) 426 kg. soybean or maize oil
   80 kg. water (approx.)
   510 kg. KOH 25° Bé red.

(3) 390 kg. soybean or maize oil
    45 kg. rosin
    70 kg. water (approx.)
  475 kg. KOH 25° Bé red.
    30 kg. NaOH 25° Bé (approx.)

(4) 155 kg. soybean or maize oil
    110 kg. sesame oil
    115 kg. linseed oil
    55 kg. rosin
    80 kg. water (approx.)
  460 kg. KOH 25° Bé red.
    45 kg. NaOH 25° Bé (approx.)

This schedule of fat charges should serve as a guide only in the selection and composition of stock for smooth soft soaps. Above all, the quantities of water mentioned should be regarded only as approximate, as it may easily happen sometimes that a deficiency, or probably an excess, of water is created in the pan by excessive evaporation or condensation. It may also happen that the amount of lye in the prescription will be excessive, which would be the case if the fats actually used contained larger proportions of unsaponifiable matter or even nonfatty impurities, water, etc.

The oils recommended in the recipes can partly or totally be replaced by the corresponding fatty acids (of linseed oil, soybean oil, peanut oil and others). Fatty acids always require somewhat greater amounts of caustic alkali than neutral oils. They may also be replaced by tall oil (see Chapter XVI). However, too high a percentage of tall oil (above 35%) tends to give soaps which leave a somewhat tacky feeling on the skin. This seems to be caused by the unsaponifiable fatty matter (about 8–10%) present in most commercial grades of tall oil. One should not forget, however, that the commercially available fatty acids may contain only about 90–95% free fatty acid, the remaining part being neutral oil, depending on origin. Distilled acids are free of neutral oil. When produced simply by splitting of soapstocks (a by-product of vegetable oil refineries) by an inorganic acid, they are composed of about 60% free acids and 40% neutral oil.

(c) *Manufacturing Process.* The whole of the fat charge is brought into the kettle, some water is added, and boiling is started with direct steam. It is advisable to withhold a small part of the fat charge for later adjustments, especially for corrections of the boil, if this proves necessary after saponification. With too large a water or caustic alkali content in the pan, addition of some fat or fat and lye may solve the problem.

The caustic lye is added in small portions only. As a principle, lye addition is continued only when the previous portions are already spent. The same considerations apply here as for the saponification of any other kind of soap; the mass must be kept homogeneous and the soap solution never allowed to separate into an open condition. This should be frequently checked by the trowel test.

When the charge contains larger quantities of free fatty acids, care must be taken to bring, at the very beginning of the boil, such amounts of lye into the kettle as would be able to prevent the mass from bunching. If this should

happen in spite of all precautions, a large portion of lye must be added to the mass at once.

When working with a fat charge composed entirely of fatty acids, it is considered a safer practice to run into the kettle first the total amount of caustic lye required and to charge the fats afterward. Such a plan prevents bunching, since the presence of excess alkali is fully guaranteed during the whole period of saponification. Mentioning saponification of the fatty acids, one may think that in the manufacture of soft soaps the use of carbonates instead of caustics would also be considered to be more expedient, as explained for the manufacture of solid soap from fatty acids. However, this is not so, as the main reason for the use of sodium carbonate instead of caustic soda was due to its comparative low cost. Potassium carbonate, however, is not cheaper than caustic potash.

In the event that neutral oils have been used, an emulsion is formed at the beginning which gradually becomes more and more viscous in the course of the process. The proper condition can be verified, since the soap mass rolls down as a homogeneous mass when tested on the heated trowel. Any separation of the soap mass, when detected by the trowel test, should be corrected by addition of a small amount of water or by boiling with open steam and continuing until a sufficient amount of water condenses to dilute the salt concentration.

When caustic soda is used with the caustic potash, it is generally not added at the beginning of the saponification process, but only after the mass becomes sufficiently viscous.

After the larger part of the lye has been used up in the course of the saponification process, the mass becomes transparent. At this stage a small sample of the mass is taken from the kettle and tried for solubility in distilled water. When a sample of the soap is not clearly soluble in distilled water, the presence of considerable amounts of unsaponified fat is indicated. Boiling must be continued with a fresh portion of lye until the test becomes satisfactory.

After saponification has been completed and no unsaponified fat is present, sufficient lye must be added to the mass to contain 0.3 to 0.6% of caustic potash. After the strengthening of the mass with sufficient free alkali is satisfactorily completed, other corrections, if necessary, may be carried out.

(d) *The Glass Test.* Samples are now taken from the boiling mass and heaped in small portions of about 2 inch diameter each on a glass plate, and their consistency observed after a short time.

(1) *Water Content.* The consistency should become salvelike rather than rubberlike, the latter condition disclosing excess water; the remedy in such cases is to put some oil, or more suitable fatty acids, from the reserve portion into the kettle and to saponify it with alkali which is added to the

kettle *before* the additional oils or fatty acids. It is possible to evaporate the excess water with indirect steam or open flame, but in most modern plants boiling is carried out only with open steam. After the amount of soap in the pan is increased by the addition of soap, the glass test should be satisfactory.

(2) *Free Alkali Content.* A smooth soft soap must contain a certain minimum amount of free alkali; this need becomes apparent when one observes a soap which is accidentally turned out as a completely neutral product. A sample of the soap is quite transparent at the beginning when heaped on a glass plate. But after a very short while the clear surface begins to display a slight glimmer in the shape of characteristic designs called the *flower* by the Continental soapmaker. However, the sample remains quite clear in the deeper layers and a turbid ring called the *lye ring* is observed only at the edges. A neutral soap displays the flower and the lye ring only to a very slight degree. Both designs appear stronger at the surface and on the edges if more free alkali is present. Both phenomena may be explained by the graining activity of the free alkali. Water evaporates at the surface and on the edges of the sample; the increased concentration of the free alkali permits graining at the surface, and in this way produces the designs.

The *flower* and *ring* constitute a good test for the proper water content of the soap as well. With insufficient water in the soap the design appears more quickly. Too much free alkali can be detected on the glass plate when the solidified drop of soap does not stick, but slides on the surface when pushed with a finger.

(3) *Unsaponified Oil.* When present, unsaponified oil causes the interior of the soap to become turbid. The detection of the presence of unsaponified oil by dissolving a sample in distilled water was mentioned earlier.

(4) *Electrolyte Content.* A sample of a soap containing too much potassium carbonate or other electrolytes remains too soft, even after cooling. On the other hand, a soap containing less electrolytes than necessary solidifies too quickly and becomes far too hard. The soapmaker used to call such soft soaps *caustic* soaps; this really means that such soft soaps were produced with caustic solutions insufficiently reduced by the addition of salts. It is comparatively easy to correct the "caustic" condition by adding some electrolyte to the soap, but it is far more difficult to amend soft soap suffering from excess electrolyte. The only remedy in such cases is to add some oil from the reserve and to saponify this portion on top of the charge, thereby diluting the electrolyte content of the soap.

The soap is now to be considered ready. After it has cooled to 65°C., the kettle contents can be emptied into suitable containers, such as barrels, drums, tank wagons. Basement rooms are most suitable for the storage of soft soaps. The temperature of the store rooms should be as low as possible, but preferably between 12 and 15°C.

The product, a pure soft soap containing a few per cent of electrolyte, is called a *soft soap base*. At this stage the product contains about 42% of fatty acids and the yield corresponds to a value of 226.2%.

In per cent, the soap yield presents the relation between the fat charge expressed as neutral oil and the mass of soap manufactured from it. In the present case, 42 parts of fatty acid is equivalent to 44.2% neutral oil. The soap yield is therefore $(100 \times 100)/42 = 226.2\%$. This means that from 100 parts of neutral oil 226.2 parts of soft soap were manufactured.

Generally, soft soap is not marketed with this comparatively high fatty acid content; it is further diluted to some extent by the addition of a small amount of electrolyte solution. The procedure of dilution is called *fitting*, but it must not be confused with the term used for the operation of separating a homogeneous soap solution into neat soap and niger. It is customary to dilute the soft soap base until it contains only 38% of fatty acids, corresponding to a soap yield of 250%. In accordance with most of the official specifications, a soft soap containing 38% of fatty acid is regarded genuine and pure.

The "fitting" operation consists of mixing into the soft soap base, at a temperature of 65°C., the analytically determined and calculated amount of liquid in the form of either a 12° Bé potassium carbonate or a 14° Bé potassium chloride solution. After this operation is finished, a final glass test and a quantitative test for free alkali content are made.

It would really be an easy thing to boil a batch of soft soap if the soapmaker could control, at any stage of the procedure, the exact quantities involved in the process. This idea is sufficiently emphasized in the description of the graining and fitting processes given in Chapter XVII. We also extensively quoted the method proposed by Wigner who first suggested the use of the manometric gage for weighing masses in the soap kettle.

It is historically interesting that as long ago as 1928 Krings[18] proposed the use of a specially constructed pan mounted on a balance for the boiling of soft soaps. The weighing could be carried out during the boil at any time. The weights could even be recorded continuously by a suitable indicating device, and the soapmaker would thereby be in a position to have the quantitative development of the boil literally before his eyes. The soapmaker could, at any moment, calculate the yield reached by the addition of fat, lye, electrolyte, water, and condensed water. He could also control the rate of evaporation by this means. Krings claimed that with such a plant the operator would be able to produce much larger quantities of soap of more uniform quality than when working with the ordinary equipment.

It is quite possible to produce soft soaps by the cold process (see Section 4 following). In the case of cold-made soft soap it is best to mix the fat charge with the calculated amount of 38° Bé KOH in the kettle. In this case

the pan should not be larger than 1–2 cubic meters and should be steam jacketed or fitted with a coil for indirect steam heating and have a stirring mechanism. After thickening, the kettle is covered and left standing overnight. The next morning, the fat charge having been saponified (as tested by the solubility in distilled water), the soap is heated by indirect steam, the necessary amount of water and electrolyte is added and the soap is adjusted to the desired fatty acid and free alkali content, etc. The use of 0.5–0.7% (calculated on the fat charge) of a saponification catalyst (such as cresol or oil of origanum) helps bring about the thickening of the soap in a very short time and accelerates the saponification process after thickening, so that often after only 4–6 hours the fat charge is completely saponified.[17]

(B) Soft Soaps from Fatty Acids

It is also possible to use fatty acids as the fat charge. In this case it is suitable to saponify the fatty acids by a kind of modified semiboiled process. The calculated amount of saponification lye is first run into the pan and diluted to a strength of about 16° Bé. The diluted lye solution is heated to about 70°C. and the melted fatty acid mixture (also heated to about 70°C.) is run into the warm lye solution, which is agitated during the process with a stirring mechanism. After complete saponification the soap is adjusted as usual to the desired fatty acid content, free alkali, etc.

Some special methods are used to produce soft soaps from fatty acids. The following process is the most convenient in nearly every respect. (See Chapter XV, 5 on fatty acids.) Saponification is very rapid and may be carried on the semiboiled system. The saponification lye and all additions of electrolyte are run into the pan together with the calculated amount of water. The amount of water must be adjusted at the end of the saponification process as already described. The lye solution is either heated to about 80°C. and the melted fatty acid stock heated to 70–80°C. run into the pan, and the procedure carried forward as described in section on semiboiled soaps, or the pan content is kept at the boil and the melted fatty acids (50–60°C.) run slowly but continuously into the pan under boiling conditions. In this case there is no agitator in the kettle. Since fatty acid saponification is strongly exothermic, the fatty acids must be added slowly to keep the process in check. The last one-fifth of the fatty acids is added especially slowly to ensure complete saponification. It is important that a surplus of alkali is always present to avoid the formation of acid soap. The final adjustment of free alkali, etc., is made as already described. In case a mixed stock of fatty acids and neutral fat or soapstock fatty acids containing less than 75% free fatty acids is used, the process is modified slightly by adding fatty acid–fat mixture in portions. Samples are withdrawn from time to time to assure that every

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[17] For unpublished results of experiments carried out by the authors, see Chap. II, 8.

portion of added fat mixture is completely saponified, as indicated by the absence of turbidity when a small sample is dissolved in hot distilled water.

The following working formula is an example of soft soaps prepared from fatty acids containing some electrolyte:

> 100 parts fatty acids
> 80 parts 30° Bé KOH diluted with 20–25 parts water
> 6.25–8.25 parts K₂CO₃ dissolved in 22–23 parts water

The resulting soap has a fatty acid content of about 45% if no water evaporates (if boiled on open flame or indirect steam) or condensate water forms (if boiled over open steam). In the latter case, 10–12 parts water are subtracted from the water in the formula to take into consideration formation of condensate.

When neutral fat replaces the fatty acids in the formula, 5% extra should be added since the fatty acid content of such material is approximately 95% due to the glyceride structure. For coconut oil the ratio is slightly higher.

There are now fatty acids on the market with very sharply defined chemical specifications (see Chapter XV). These fatty acids are especially suitable for the production of soft soaps. All that has been pointed out about the advantages of the use of fatty acids (Ch. XV, 4) instead of neutral fats holds good for soft soaps as well. But some disadvantages of fatty acids for soft soap manufacture should not be overlooked. The glycerine present in soft soaps from neutral fats acts as a humectant, thus retarding evaporation of water. Fatty acids, especially unsaturated fatty acids, are also very reactive, discoloring badly if not stored in proper containers and turning rancid with exposure to air. If such spoiled or discolored fatty acids are used, only low-grade soaps may be expected, since little can be done to improve such products after saponification. As previously pointed out, tall oil has recently been used to replace more expensive fatty acids and oils. Tall oil should be considered as fatty acid and saponification carried out accordingly.

(C) Bleaching of Soft Soaps

Bleaching of the soft soap is most conveniently carried out when adjusting the soap to the desired fatty acid content. The best agent is a chlorinated bleaching liquor (potash bleach or a potash-soda mixed bleach, see Chap. X, 1, B). This operation is preferably carried out at 40–50°C. to obtain the most powerful action. It is advantageous to treat the product with the bleaching agent in an enameled kettle, or other lined vessel resistant to free Cl_2. The bleaching action arises from the active chlorine (present in the hypochlorite liquor) which, in its nascent form, has a very energetic bleaching effect upon soap. The temperature of the soap should be low, but should in no case exceed 60°C. Low temperatures permit more complete utilization of the bleaching power of the liquor. Each 1000 kg. of soap needs 6 to 25 kg.

of 25° potassium hypochlorite lye, which is diluted to 12° Bé. The available chlorine in this dilute bleaching lye should be about 6–7%. The bleaching liquor is slowly added to the soap with constant stirring. Stirring is then continued for another fifteen minutes or so, after which the mass is allowed to stand for about half an hour.

After the bleaching process, the free alkali is again determined. When bleaching with alkaline lyes the soap should not be made too alkaline. In fact, any additional lye should be introduced after or during the bleaching process.

TABLE XIX-4

DETAILED REQUIREMENTS FOR AUTOMOBILE SOAP (PS-598)

Detailed requirements	Min.	Max.
Moisture (toluene distillation method), %	—	55
Total matter insol. in alcohol, %	—	1.0
Free alkali, calc. as KOH, %	—	0.1
Free acid, calc. as oleic acid, %	—	0.2
Alkaline salts, calc. as K_2CO_3, %	—	0.2
Matter insol. in distilled water, %	—	0.2
Chloride, calc. as KCl, %	—	0.5
Unsaponified and unsaponifiable matter, %	—	1.0
Anhydrous soap, calc. as potash soap, %	43	—
Total sodium compounds, calc. as Na_2O, %	—	0.5
Glycerol, %	—	0.8
Iodine number (Wijs) of mixed fatty acids derived from the soap	175	—
Acid number of mixed fatty acids derived from the soap	190	205
Rosin	—	None
Sugar	—	None

∗ ∘ ∘ Other bleaching agents are seldom used for soft soaps. Sodium hyposulfite, a reducing agent used by some manufacturers, has the advantage that it may be used without waiting for the soap to cool. It is simply added in a concentrated solution or even as fine powder to the ready boiled soap. About 0.25–0.5% of sodium hyposulfite should be sufficient.

(D) SPECIFICATIONS FOR SOFT SOAPS

It is of importance to note that the U. S. Federal Specification Board gives a specification for *Potash linseed oil soap, liquid or paste, for floor and general cleaning (PS-603)*, which practically excludes the use of such electrolytes as K_2CO_3, KCl, etc.

Specification PS-598 for liquid or paste soap for automobile, floor, and general cleaning contains the detailed requirements shown in Table XIX-5.

As a matter of fact, consistency requirements are not so severe and such soaps are not difficult to produce. With the prescribed minimum content of

anhydrous soap these products are practically all in the form of a paste or at least a very viscous liquid soap.

A much less strict definition for *Soft soap* is proposed by the National Association of Insecticide and Disinfectant Manufacturers in the United States as follows: "Soft soap is the product derived from the action of a solution of potassium hydroxide with or without sodium hydroxide and potassium silicate on fats, oil, or resins, or any mixture of same. It shall contain not less than forty parts per centum of fatty and resin acids, of which not more than one-third may be resin acid. It shall contain not more than three parts per centum of silicates, calculated as sodium silicate ($Na_2O \cdot 3SiO_2$)."

Here, even filling with silicates is permitted.

TABLE XIX-5

DETAILED REQUIREMENTS FOR AUTOMOBILE SOAP (PS-598)

Detailed requirements	Min.	Max.
Moisture (toluene distillation method), %	—	60
Total matter insol. in alcohol, %	—	1.0
Free alkali, calc. as KOH, %	—	0.1
Free acid, calc. as oleic acid, %	—	0.2
Alkaline salts, calc. as K_2CO_3, %	—	0.2
Matter insol. in distilled water, %	—	0.2
Chloride, calc. as KCl, %	—	0.5
Anhydrous soap, calc. as potash soap, %	40	—
Total sodium compounds, calc. as Na_2O, %	—	0.5
Glycerol (% of anhydrous potash soap)	—	0.8
Iodine number (Wijs) of mixed fatty acids derived from the soap	100	—
Rosin, %	—	6
Sugar	—	None

(The specification of the U. S. Pharmacopeia for soft soap is dealt with in Chapter XXII on medicated soaps.)

British Specifications are set forth in *Government Department Specifications for General Stores*, published by H. M. Stationery Office, 1929 (reprinted 1945). The specifications for grade I (resin free) and grade II soft soaps are as follows:

1. The soap shall be free from objectionable odors, and shall not develop such odors during storage within twelve months of delivery. Any fish or marine animal oil used in manufacture shall be deodorized. Scenting material shall not be used.

2. The soap shall not become liquid at a temperature of 90°F. and no liquid shall separate from them when cooled to a temperature of 32°F. for 24 hours.

3. The grade I soap shall be made from seed oils and potash; shall be free from resin; and shall yield not less than 38% of fatty acids.

4. The grade II soap shall yield not less than 40% of mixed fatty and resin acids. The resin acids shall not exceed 25% of the total fatty and resin acids.

5. In soap of either grade the total impurities shall not exceed 4%, and the free alkali, caustic, and carbonate (calculated as K_2O) shall not exceed 3%, of which the free caustic (calculated as K_2O) shall not exceed 0.75% on the soap.

(E) "Fig" Soaps

As already pointed out, *figged* and *silver* soaps are losing their popularity and we will therefore deal with these types of soft soaps in a more summary manner.

Fig soaps are those soft soaps which gradually develop what appear to be starlike crystals from the sides to the center of the soap, a change which is termed *figging*, and which has been generally attributed to crystallization of solid soaps of the harder fatty acids from out of the colloidal mass of the soap. This crystallization is possible only if no sodium salts are present in the lyes used; otherwise silver soaps will result with approximately the same fatstock (see Part F). The choice of a correct fatstock is the primary condition for the preparation of a good fig soap. If darker oils and fats are used, a fig soap results in which the figging is embedded in a light to dark yellow transparent mass; if very light oils are used the soap appears very light colored or even colorless, usually with a very faint greenish gray tint. For the darker type, crude palm oil is a valuable raw material.

Examples of fatstock compositions are:

For summer:

(a) 49% tallow
   1% palm oil
  17% cottonseed oil, refined
  33% soybean oil, refined

(b) 35% tallow
   3% palm oil
  22% horse fat
  40% linseed oil

(c) 36% tallow
   2% palm oil
  17% lard
  15% cottonseed oil, refined
  30% soybean oil, refined

(d) 46% tallow
   4% palm oil
  25% soybean oil
  25% corn oil

For winter:

(a) 33% tallow
   3% palm oil
  16% cottonseed oil
  48% soybean oil, refined

(b) 36% tallow
   3% palm oil
  61% soybean oil, refined

(c) 28% tallow
   2% palm oil
  15% lard
  55% soybean oil

(d) 31% tallow
   4% palm oil
  33% olein (red oil)
  32% soybean oil

A technical grade of tallow may be used.

It is important that only potassium carbonate (K_2CO_3) be used as electrolyte. In the summer, 19 parts K_2CO_3, and in the winter, 22 parts K_2CO_3,

are used for every 100 parts caustic potash (KOH) 50° Bé. The lye is di-
luted to about 30° Bé strength. Fig soap is boiled similarly to common soft
soap, but is usually prepared with less free alkali. Bleaching—if any—is
carried out as for common soft soap. The general fatty acid content is about
38–39% or occasionally higher, with yields running 240–250% of the fat
charge. The soap is stored in containers at 12–20°C. for 3–6 weeks to com-
plete figging.

According to Krings[18] a good figged soap requires: (1) the caustic pot-
ash and the electrolytes used to be free of sodium compounds; (2) free al-
kali to be well adjusted (about 0.25–0.3% free KOH); (3) the amount of
noncaustic electrolytes to be within the limits given above; acid content to
be above 38%; (5) the percentage of fats containing stearic acid to be as
high as given in the formulas above; (6) the fat charge to be completely sa-
ponified; and (7) temperature during the crystallization period to be as
constant as possible.

A figged soap may also be produced by incorporating into a common
transparent soft soap a hard soap cut into small pieces the size of the natural
fig,[19] which incidentally is a good method of using hard soap scrap.

(F) "SILVER" SOAP

Silver soaps with a mother-of-pearl sheen are based on similar fatstock
formulas as for fig soaps. In our opinion, these soft soaps are more impor-
tant than fig soaps. They are more easily produced and need not be stored
for such extremely long periods of time to develop the desired mother-of-pearl
sheen. Silver soap can be produced on a more economical basis than figged
soaps, with inexpensive hard stock such as hardened fish oils.

In principle, silver soaps are produced in a similar manner to common
soft soaps. They are usually prepared with a low percentage of free alkali.

Mixed alkalis are used (10–35 parts of a 30° Bé solution of NaOH to 100
parts of 50° Bé KOH containing 20–25 parts of K_2CO_3). The mixture of
NaOH, KOH, and K_2CO_3 is diluted to about 30° Bé if open steam coil heating
is used, or to 20–22° Bé if saponification is carried out over a direct fired pan.

Illustrative examples of fatstock compositions follow:

For summer:

(a) 65% cottonseed oil, refined	(b) 50% cottonseed oil, refined
10% soybean oil	15% linseed oil
25% tallow or hardened fish oil	28% tallow
	7% coconut oil

[18] R. Krings, *Die zeitgemässe rationelle Herstellung der Schmierseife,* Allgemeiner
Industriekatalog, Berlin, 1928, pp. 66–67.
[19] German Pat. 415,964.

(c) 50% cottonseed oil, refined
    45% lard
    5% tallow

(d) 50% cottonseed oil, refined
    30% tallow
    10% palm oil, bleached
    10% lard

(e) 50% tallow
    45% lard or bleached bone fat
    5% coconut oil

For winter:

(a) 65% cottonseed oil
    15% groundnut oil
    20% lard

(b) 80% cottonseed oil, refined
    20% tallow or hardened fish oil

(c) 55% cottonseed oil, refined
    25% groundnut oil
    12% palm kernel oil
    8% palm oil, bleached

(d) 65% cottonseed oil, refined
    25% horse fat
    10% tallow or hardened oil

(e) 35% cottonseed oil, refined
    25% soybean oil
    35% tallow or hardened oil
    5% coconut oil

Fatty acids blended to give the corresponding compositions may replace the neutral fats and oils. Tall oils in various stages of refinement are commonly used and may replace part of the more expensive oils or fatty acids (see above).

(G) Building and Filling of Soft Soaps

Building up of soft soap may be carried out with addition of sodium or potassium silicates, but filling with flour, starch, etc. is not advisable as it impairs the transparent appearance (except in the case of silver soaps, where this would not be a handicap). Generally speaking, the correct amount of electrolyte is filling enough, and special additions should be made only if they improve the detergency of the soap. Here, sodium silicate in percentages of 5–10% (calculated as a 30° Bé solution) is a suitable soap builder. For fig soaps, potassium silicate solutions are used to avoid disturbing the figging.

Methylcellulose or C.M.C. is used as a filler for soft soaps (see Chapter XI). Methylcellulose and C.M.C. have the advantage over many other organic fillers in that they do not impair the transparency of the soap. The following formula for their use is given as an example:[20]

(a) Fatty acids .... 1000 lbs.
    Potassium hydroxide (50° Bé) .... 370 lbs.
    Sodium carbonate .... 42 lbs.
    Sodium hydroxide .... 24 lbs.
(b) Potassium chloride (20° Bé) .... 50 lbs.
    Potassium carbonate (36° Bé) .... 25 lbs.

[20] H. Bennett, *Formulas for Profit*, World Pub. Co., New York, 1942, p. 485.

(c) Methylcellulose solution _____ 500 lbs.
(d) Sodium hydroxide (38° Bé) _____ 25 lbs.

Prepare (a) in the usual fashion, adjust to 40% fatty acids, and treat with bleach lye. Add (b), and to this, in alternative small portions, (c) and (d). The soap resulting should have 32 to 33% fatty acids.

The methylcellulose solution is prepared as follows:

(a) Water _____ 200 lbs.
     Caustic KOH (38–39° Bé) _____ 40 lbs.
(b) Methylcellulose _____ 40 lbs.
(c) Water to make _____ 1000 lbs.

To the boiling mixture (a) add (b) with stirring. Let stand and swell for about ½ hour. Stir in (c) ice cold. Let stand overnight and stir again.

C.M.C. solution, prepared in about the same proportions as methylcellulose solution, are somewhat easier to prepare. C.M.C. may be simply dispersed in cold water until, after some hours, a gel forms. The gel may then be heated to about 70–80°C. and left standing overnight.

(H) Modern Developments

Soft soaps occupy an important place in the industrial use of soaps in Europe and the United States. Hitherto, however, they have not made the same headway in tropical lands. The advantages of easily soluble and measurable soft soaps in laundry work are sufficiently marked to lead one to expect that soft soaps would be likely to control a good proportion of the tropical soap trade if they could be made to withstand the climatic changes and the great heat without altering consistency. Work has been proceeding for some years on the production of a soft soap for use in tropical countries. But still other factors enter into the problem. To acquire and retain a salve-like consistency, an ordinary soft soap must contain a relatively large excess of free alkali, which excludes its use in the laundering of fine textiles.

Particularly significant in this field are the investigations and patents of F. W. Leffer. His patents are based mainly upon the saponification of fats under increased pressure at temperatures above 100°C. According to British Patent 378,913, fatty oils (soybean, linseed, groundnut) are saponified under those conditions with a mixed caustic lye in which the ratio of caustic potash to caustic soda does not exceed 90 : 100. Alkali salts (sodium or potassium chloride, carbonate, sulfate, or their solutions) are also added in the proportion of 2 to 6%, either to the raw material, or, preferably, to the saponified mass. In this way a smooth salve-like consistency is acquired.

The same inventor (Brit. Pat. 375,914) improved and supplemented the process in the following details: Fats or oils are heated under high pressure

and at a temperature of 100 to 250°C. with a mixed caustic lye in which the ratio of caustic potash to caustic soda does not exceed 90 : 100. The lye may also consist in the main or exclusively of caustic soda. When saponification is complete, the soap is neutralized with the requisite quantity of alkali or fatty oil. Alkali salts may be added to the saponification mixture.

Further modifications in the process, disclosed in German Patent 598,627 of the same inventor, cover the following claims: (1) In a process for making hydrocarbon-containing soft soaps by pressure saponification at temperatures exceeding 110°C., the soaps contain not less than 2% hydrocarbon oils, and not more than 1% alkali salts calculated as anhydrous salt upon the total weight of the soap mass. (2) In a process according to claim 1, when using 0.2 to 0.8% alkali salts the soap mass receives the addition of 3.2 to 4.5% of a petroleum jelly-like hydrocarbon oil. An important feature is the inclusion of unsaponifiable mineral oils. Among the salts specified are $NaCl$, KCl, $Na_2CO_3 \cdot 10H_2O$, $K_2CO_3 \cdot 2H_2O$, $Na_2SO_4 \cdot 10H_2O$, $Na_2SiO_3 \cdot 9H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, and $Na_3PO_4 \cdot 12H_2O$. They are applicable singly or in mixtures.

The object of the salts and the petroleum jelly, etc., is to impart the right salve-like consistency to the neutral soap. Whereas the ordinary commercial soft soaps prepared without pressure rarely contain less, and usually more, than 0.4 to 0.6% free alkaline hydroxide, soaps can be made by the new process with a free alkali or free acid content of less than 0.01%.

Regarding the ratio of mineral oil to salts and the influence on the total fat percentage in the soap, the specification continues: In the process at least 2%, and preferably 3.2 to 4.5% hydrocarbon oil is applied, together with a proportion of salt which, calculated as anhydrous salt, may be reduced to 0.2%. The preferred salt content of a neutral, salve-like soft soap of 37 to 39% fatty content, containing 3.5 to 4% hydrocarbon oil, is about 0.3 to 0.8%.

With simultaneous addition of a salt solution and of a hydrocarbon oil, it was found that with various soap batches the quantities of salt and hydrocarbon needed to impart the desired properties also varied. A change in the salt content of 0.1% without any change in the hydrocarbon content frequently had a perceptible and sometimes a marked effect upon the consistency, the congealing point, and other physical properties of the soap. In the case of soft soaps with a low fat content, e.g., less than 36%, it is advisable to employ more hydrocarbon oil and less salt than in that of soaps with about 38% fat. But for soaps with more than 39% fat, the salt may be increased with advantage, while reducing or leaving unchanged the hydrocarbon oil proportion. In its essence, the German patent corresponds to the two British patents.

The production of soft soaps by saponification with caustic soda lye is also noteworthy. This is a feature of German Patent 571,738. Here, a soda

soap is intimately mixed with an alkali metaphosphate, and water is run in to give the desired consistency during the mixing. Small amounts of other alkali phosphates may be incorporated at the same time.

Soft soaps also form bases for all sorts of cleansing pastes, with the addition of scouring agents and solvents. (These products are dealt with in Chapter XX on solvent soaps, special cleaners, etc.)

Often, soft soaps are perfumed with such inexpensive materials as citronella oil, nitrobenzene, and camphor oil. Coloring may be done by adding water-soluble yellow, reddish, or green dyestuffs. Crude palm oil within the fat charge imparts to the soap the natural orange color of the oil, which is especially desirable in common transparent soaps or darker grades of figged (German *Elain*) soaps.

(4) Manufacture of Soaps by the Cold or Semiboiled Process

This section deals with a method of soap production especially suited for smaller factories because of the small initial outlay required for the plant. Not only do soaps made by the cold process require a moderate size plant, but the operation itself is simple and speedy. This chapter describes mainly the practical side of the process involved.[21] The theoretical aspects of this saponification process are described in Chapter II, 7 and 8.

(A) THE COLD PROCESS

The saponification process as well as the equipment is extremely simple. The equipment consists of a kettle in which the fats are melted. A double-jacketed vessel is the most suitable for this purpose, one that can be heated by steam, hot water, or electricity, so as to avoid local overheating of the fats. The lye and fats are stirred together with a good mechanical stirrer, preferably constructed so that it can be lifted out and the kettle tilted. A fixed stirrer, however, is acceptable if the kettle is provided with a large bottom opening, out of which the thickening soap mass can be poured to the frames. The latter are constructed either of wood or of iron, and can be taken apart to facilitate removal of the solidified soap. Frequently they are portable. A complete setup for cold process soaps is shown in Fig. XIX-1.

Formerly, only coconut and palm kernel oil were saponified by the cold process, with the inclusion at the most of a small percentage of vegetable oils, especially castor oil. The latter actually speeds up saponification owing to low sensitivity of sodium ricinoleate to electrolytes, presence of OH groups in the triglyceride molecule, and its viscous character. It is now recognized that not only coconut and palm kernel oils but other fats can be saponified by the cold method. Only pure fats are used in the production of cold-

[21] J. Davidsohn and A. Davidsohn, *Soap, Perfumery and Cosmetics, 11*, 601–605 (1938).

stirred soaps, since impurities cannot be eliminated by salting-out as in the case of boiled soaps. An important factor in this connection is the correct choice of starting temperature, which depends upon the melting point of the raw fats.

The question now arises: How is it possible that the great excess of electrolyte at the start of the saponification process does not, as was formerly assumed, entirely suppress the saponification reaction? In saponification by the cold method we use concentrated lyes (generally 38° Bé caustic soda). Even before the commencement of saponification and pastiness the mass is in a thickly viscous condition. It is this thickly viscous condition that hinders salting-out of the resulting soap, so that the emulsifying action of the soap at first produced only in traces is maintained in spite of the high electrolyte
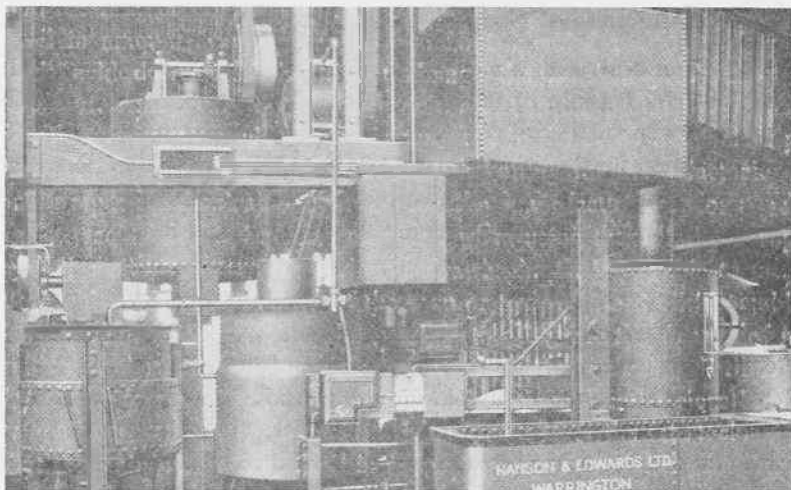
Fig. XIX-1. Complete set-up for cold process soaps at Hanson & Edwards, England.

concentration. Moreover, the intensive stirring treatment applied in cold-process saponification continually keeps any separated soap in intimate contact with the still unsaponified mass. Moreover, still other factors come into play: the velocity of salting-out and the speed of saponification.

Given a low salting-out speed and a high saponification speed, a good saponification ensues; conversely, complete saponification is, at the very least, rendered doubtful. But the salting-out velocity also increases, quite apart from the electrolyte concentration, when the mass in which salting-out occurs is less viscous. This also explains why, in our own experiments using dilute 15° Bé caustic soda, complete saponification was not attained even though conducted with an excess of lye or no excess of lye.

Nowadays, various methods are available for securing a viscous condition

after mixing the melted fats with lye. This condition really represents a state of emulsification which is always accompanied by a change in viscosity. There is the possibility of using powerful and efficient agitators which are now available. Second, we may point to the addition of catalysts (see Chapter II, 8), or the addition of soap to the lye–fat mixture. A marked increase in the speed of saponification may be secured by adding 0.6% soap (calculated upon the fats), in solution form, to the fat–lye mixture.

After thorough emulsification has taken place, the mass is run into the frames, where final saponification takes place with the evolution of more heat. The thickened or emulsified condition is best recognized if the homogeneous soap mass dripping from a wooden spatula onto the surface of the mass in the kettle remains on top for a short time so that a clear pattern is traced by the dripping sample.

It sometimes happens that the soap mass is prematurely transferred to frames. This happens especially when working in cold rooms, and solidification of the soap mass in the kettle by the cold gives the appearance of soap formation. If it is found that the temperature of the mass is below the melting point of the fat mixture being saponified, it is not transferred to the frames, but instead the whole kettle is warmed, preferably by slow indirect heating, until the contents have liquefied and the soap mass no longer solidifies. Reheating is naturally a simple matter when using a jacketed kettle heated by water, steam, or electricity. This is particularly convenient in the case of high-melting fats.

It is essential that the actual attainment of soap formation be recognized. If the soapmaker cannot establish this point, he should stir a few kilograms of the fats with the requisite quantity of lye in a basin at the appropriate temperature (see above), and by his small-scale trial he may acquire the knack of recognizing when the soap has formed. Once the soap in the basin has reached the thickening point it is carefully wrapped in cloth and left in a warm place (about 40°C. or even higher in the case of higher melting fats) to complete saponification. Such experiments prevent large-scale failures.

When dealing with high-melting fats it is good practice to leave the frames with the soap mass in a warm place for some time before letting them cool. Care should be taken that the spontaneous heating in the frames does not go too far, the temperature being tested to make certain that it does not exceed 90 to 95°C. If this should happen, the contents are stirred or, in extreme cases, the outsides of the frames are cooled with water.

It is a mistake when using coconut oil or palm kernel oil alone to permit too rapid a saponification which results in a gray and unattractive soap. In summer, therefore, or when operating in warm rooms, it is advisable not to raise the temperature above 32°C. before stirring in the lye. It is particularly important in the case of coconut oil that the latter should not have an

unduly high acid value, because such an oil will saponify rapidly and yield a coarse grained soap.

Since, as already mentioned, the saponification is completed in the frame, no opportunity arises for correcting any defects in the frame itself.

It is interesting to note that, in recent experiments by E. J. Better and A. Davidsohn (unpublished) in the laboratory of Palestine Oil Industry "Shemen" Ltd., Haifa, it was found that in the emulsification only 1.2–1.7% of the neutral fat is saponified. The method of proving this interesting fact is as follows. A weighed sample from the mass in the kettle is dispersed in a large excess of hot water. To this is added a surplus of HCl and the product is extracted with ether as described in Chaps. XXXVII and XXXIX on analytical methods. After evaporating the ether and weighing to constant weight, the fat extracted is dissolved in a neutralized mixture of 1 : 1 ether : alcohol and titrated with 0.1 N NaOH to obtain the acid value. This shows how much fatty acid was saponified at the stage of "thickening." If the fat charge was neutral it was neutral fat which was saponified, but if the fat charge was acid these fatty acids were saponified first plus a certain amount of neutral fat, which my be calculated from the difference between the acid value of the split sample withdrawn from the kettle after thickening and the acid value of the initial fat charge.

An important question in the production of cold-made soaps is saponification with less lye than that required theoretically. This leaves a certain amount of neutral oil in the product which decreases brittleness and ensures an alkali-free product. Any harshness of the soap can be overcome by superfatting agents. Using the calculated quantity of lye, it is almost impossible to dispense with a small-scale test, for only thus can it be ascertained whether the amount of lye is too small, or, more dangerous, too high.

One can nevertheless turn out a satisfactory soap with a calculated amount of lye and even without a superfatting agent by using a fat mixture containing only 30% coconut or palm kernel oils. The skin-irritating effect is actually inherent in the nature of the soaps from coconut or palm kernel oils (see Chap. XXXII). This defect can be obviated by three different methods: (1) by incomplete saponification of the fats; (2) by superfatting the completely saponified soap; and (3) by using not more than 30% coconut or palm kernel oils in the fat mixture.

In this connection it is important to examine the form in which the unsaponified portion of the fats is present in the final soap. This question has been examined from various angles.[22] It may be assumed that the unsaponified fat is present not as ordinary triglyceride, but as mono- and diglycerides which do not reduce lathering power to nearly the same extent as would the triglycerides if present in the soap as unsaponified fat.

[22] J. Davidsohn and E. I. Better, *Fettchem. Umschau*, *40*, 26–30, 52–55 (1933). J. Davidsohn, *Seifensieder Ztg.*, No. 18 (1934).

In practice, there is actually no great difference between the lathering powers of a fully saponified coconut soap and a not quite completely saponified coconut oil soap made by cold process. It could be proved that this point applies not only to coconut soaps, but also to cold-made soaps from other fats. This observation is of economic as well as scientific importance, for it is an advantage if soaps can be made by the cold method with less than the calculated quantity of lye, and fulfil all requirements. The result is of scientific interest because of the fact that the cold-process saponification —particularly with coconut and palm kernel oils—results in partial saponification of the triglyceride molecule of the unsaponified portion of the fat.

The formulas that follow are calculated on the basis of the average saponification value of the fat mixture undergoing complete saponification. If it is desired to leave a small percentage of the fats unsaponified, it is merely necessary to make the equivalent reduction in the quantity of lye. In all cases, however, the operation must be controlled by laboratory analysis. Several of these formulas also contain caustic potash. The addition of from 20 to 25% caustic potash to the caustic soda renders the soap less brittle and improves its softness and lathering power, particularly when hard fats are used mainly or exclusively. Cold-process soaps may be made according to the following formulas:

Coconut oil	45 kg.
Castor oil	5 kg.
Caustic potash, 38° Bé	4 kg.
Caustic soda, 38° Bé	25 kg.

Coconut oil	25 kg.
Tallow	25 kg.
Caustic potash, 38° Bé	5 kg.
Caustic soda, 38° Bé	22 kg.

Coconut oil	35 kg.
Olive oil	7.5 kg.
Groundnut oil	7.5 kg.
Caustic soda, 38° Bé	27 kg.

Coconut oil	25 kg.
Lard	15 kg.
Olive, groundnut, or sunflower oil	10 kg.
Caustic soda, 38° Bé	26 kg.

(B) Filling of Cold-Made Soaps

It is quite possible to produce a cold-process soap filled with sodium silicates. The Philadelphia Quartz Co. recommends the following formulas and procedure.

> 75 parts tallow
> 25 parts coconut oil
> 75 parts caustic soda lye, 35.5° Bé

125 parts "N" silicate of soda*
300 parts soap

75 parts tallow
25 parts coconut oil
70 parts caustic soda lye, 35.5° Bé
100 parts "N" silicate of soda
270 parts soap

It is advisable to use only high-grade tallow. If the tallow contains connective tissue or other impurities, it should be boiled on salt brine and allowed to settle.

Three weighing tanks are usually arranged: (*1*) to supply the exact amount of fat stock; (*2*) for the exact amount of lye; and (*3*) for the silicate.

The whole amount of fat charge is first run into the crutcher or into a kettle fitted with an agitator (145–150°F. in cold weather, 125–130°F. in summer). The crutcher is started and then all the lye is quickly run into the grease. This should take not more than two minutes. The mixture is crutched rapidly until it begins to thicken. At this time, considerable heat is liberated by the reaction between the stock and the caustic. If necessary, cold water may be run through the crutcher jacket to prevent temperatures over 200°F. from being reached, although this is not usual with tallow. The silicate is added quickly while the crutcher is running. At first the mixture becomes thinner, but the crutching is continued and in a few minutes the whole mass gradually turns creamy.

It is important that the silicate should not be added before thickening has occurred; otherwise saponification becomes difficult. On the other hand, the silicate solution must be run into the soap mass in a fast and steady stream, or the soap may become too thick and the silicate not distributed homogeneously. The filling of cold-made soap is rather difficult and in general it is advisable to produce filled soap by the semi-boiled process rather than by the cold process.

(C) PERFUMING AND COLORING

When perfuming and coloring cold-made toilet soap it is important to take into consideration the fact that, in contrast to perfuming and coloring milled toilet soap (when perfuming and coloring takes place during the milling process), cold-made soaps are generally perfumed and colored when soap formation begins. If a coconut oil is used with a somewhat high content of free fatty acids, it is advisable not to add the color immediately before framing, but to stir it beforehand into the oil. The same applies to the perfume. The point to be remembered in connection with the perfume is that a considerable proportion may be attacked by the free alkali which remains

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* A solution of 37.6% ($1Na_2O : 3.22SiO_2$). See Chapter IX, 4.

in large excess in the mass for a considerable time, until it is completely bound with the fat after spontaneous heating. In this process the perfume frequently suffers unwelcome changes; among the alkali-sensitive perfumes are many esters, such as benzyl acetate and ethyl acetate.

Perfume and color may be incorporated with cold process soaps in the final, and still liquid, soap paste.

In coloring the soap it should be noted that it is best to prepare a dye solution by boiling the dyestuff for a few minutes in water, and filtering through cloth. Such a solution is best kept in stock.

For perfumes most suitable for perfuming cold-made soaps, see Chapter XXV. Fournét[23] gives a list of alkali-resistant perfumes:

Alcohols
   terpineol
   geraniol
   citronellol
   rhodinol
   phenyl ethyl alcohol
   linalool
   sentalol
Ketones
   ionone
   methylionone
   methylacetophenone
Phenyl ethers
   safrole

   isosafrole
   hydroquinone dimethyl ether
Naphthyl ethers
   yara-yara (2-methoxynaphthalene)
   bromelia
   diphenyl ether
   phenyl methyl ether
   benzyl methyl ether
   bromostyrene
Esters
   benzyl benzoate
   benzyl cinnamate
   methyl cinnamate
   ethyl cinnamate
   bornyl acetate

Coumarin and amyl cinnamaldehyde are also relatively resistant. Ethyl and amyl salicylates not only are alkali resistant but have a strong catalytic effect during the saponification process (see above).

(D) SPECIAL PROCESSING OF COLD-MADE SOAP

We have mentioned that *superfatting* of cold-made soaps is very often advisable. As superfatting agents, only those of a genuine fatty nature, and not starch etc., should be used for this purpose. Vaseline and lanolin as well as fatty alcohols such as ethyl alcohol are suitable in percentages of 2–4% (calculated on the soap). If superfatting agents are added it is possible to saponify the fat charge more completely. The superfatting material is dissolved in the fat charge before adding the saponification lye.

An important factor for the manufacture of cold-made soaps is to prevent the sticking of cooled soap to the sides of the frames. It has been found practical to cover the inside of the assembled frames with parchment paper or, better, with paper soaked in molten paraffin wax. These papers can be re-

[23] R. Fournét, *Seifensieder Ztg.*, 65, 381, 400 (1938).

moved very easily from the cooled soap and can even be used again for an-other charge.   Another method is to cover the sides with light cotton cloth. This can also be removed easily from the soap and re-used many times.

The usual method of forming cold-made soaps is by wire cutting the solidified soap blocks removed from the frames into slabs, and finally into tablets of the desired size, and shaping these tablets as usual.   However, it is possible to transform the blocks into flakes, then to dry the flakes, to mill and plod them as common toilet soaps.   In this case perfumes, color, and even superfatting agents may be added during the milling process.   Pure coconut oil soaps are not suitable for this process, as they are too brittle to be milled and plodded.

Another method of processing cold-made soap further is to dissolve the still warm, but completely saponified, soap in water containing some caustic alkali, to grain-out the dissolved soap on spent lye, or to fit the soap on niger. In this case a soap is obtained which may be treated as a common curd soap base.   This, as a matter of fact, is not possible with coconut oil soaps, which require too much electrolyte for salting-out.

A difficulty in the cold saponification process is the incorporation of scrap from the cutting of previous charges.   The best way is to incorporate the scrap into a charge of a semiboiled soap.

Very frequently, cold-made soaps are aerated in the crutcher to produce floating soaps.   This is done by adjusting the height or volume of the mass in the crutcher so that by reversing the worm the soap just flows over the top into the helix.   With coconut oil soaps containing 55–65% pure soap content, where saponification may be allowed to proceed to some degree, the soap may be aerated to a density as low as 0.6% without difficulty.   Another method of aerating cold-made soap is to add a small amount of aluminum powder dur-ing the initial stage.   The alkali forms sodium aluminate, liberating hydrogen, which in turn aerates the mass.

(E) THE SEMIBOILED PROCESS

This is a modification of the cold process for soaps that is best adapted to the production of soaps from mixed fats of higher melting point.   In this process both fatty acids and rosin can be included in the fat charge.   In brief, the method involves the same operation as in cold saponification, except that the temperature lies between 70 and 80°C.   The liquid fat mixture hav-ing been brought to this temperature, possibly with the addition of some melted rosin, the requisite quantity of lye is introduced and stirring is con-tinued until the soap is formed.   Care should be taken that the temperature of the mix does not fall below 70°C.   With a higher percentage of rosin or fatty acid, the fat mixture at 70 to 80°C. is run into the lye to avoid formation of lumps.   After stirring with sufficient thoroughness, the mass is left for

one half to one hour while saponification proceeds. When saponification has advanced sufficiently, the filler solution is added, as in the case of cold-made soaps, if such an ingredient is used. Saponification then proceeds to completion and the soap mass forms a liquid paste. If the paste is not sufficiently liquid, a little common salt may be added (0.3–0.5% calculated on the fat, 0.3% for an electrolyte-sensitive fat mixture, and up to 0.5% for a less sensitive material). Unless a floating soap is desired, care should be taken that no air is included when stirring, for the soap paste would then be rendered frothy.

Adjustment of the alkali content (free alkali) can be effected after complete saponification (a sample of the soap mass should give a clear solution in hot distilled water) either by adding lye or (when the phenolphthalein test indicates a large excess of lye) by adding fatty acid. The possibility of such an adjustment is clearly a great advantage over cold-process saponification. Another advantage of semiboiled saponification is the opportunity of previously dissolving waste soap from cuttings, etc. in the lye. It is true that, with very skillful operation, soap cuttings can also be included during saponification by the cold process. If cuttings of soap made by the cold process are in stock it is recommended that an occasional batch be prepared by the semiboiled process in order to utilize this waste material. When saponifying difficultly saponifiable fat mixtures (high tallow content) the temperature often drops too sharply, in which case it is necessary to increase the temperature. Semiboiled process soaps are now rarely run into small frames to complete the saponification because the advantageous possibility of adjusting the alkali content is thereby ruled out. It is more usual to charge the finally saponified soap paste through the crutcher into frames, which may be considerably larger than those used for cold-process soaps.

At this juncture we may add that saponification by the cold or semiboiled process is also applicable to the production of liquid soaps, shaving soaps, and shaving creams (Chapter XXI).

Following normal practice with semiboiled soaps, the size of the fat charge may be considerably greater than in the case of cold-made soaps. But this naturally does not exclude the possibility of running smaller batches. Practically every fat combination may be used as fat charge for the semiboiled process.

The addition of potassium carbonate as filler has the effect of producing a soap of somewhat softer texture.

A useful description for the manufacture of a filled semiboiled soap is given by Philadelphia Quartz Co.: 315 parts tallow, 55 parts coconut oil, 280 parts caustic soda lye (35° Bé), and 185 parts "N" silicate of soda. The stock is warmed to 140°F. and the lye and the silicate are added as described in the cold process. Some soapmakers prefer to mix the silicate with the lye

and add them together. As soon as the silicate or the silicate and lye is thoroughly mixed with the stock, agitation is stopped and the mixture is allowed to stand for 1–1.5 hour. The temperature should then be about 180°F. Steam is used to bring up the temperature if necessary. The crutcher or agitator is next started slowly. After 10–15 minutes, alkalinity of the soap can be adjusted by the addition of 8° to 10° Bé lye or of coconut oil. When the materials have combined into a homogeneous mass, the soap is run into a frame or frames. Further mixing here may be necessary to prevent the formation of streaks. It is desirable to reduce the temperature until the mixture will just discharge from crutchers without sticking. This will prevent separation in the frames.

Care is necessary to prevent crutching too much air into the soap in the semiboiled process. The movement should be slow. In the center-well type of crutcher, the tube should be covered with the soap batch to avoid trapping air in the soap thrown out by the screw.

The semiboiled process is especially suited for the production of filled soaps. The following formulas illustrate this point.

FORMULA 1

Palm kernel or coconut oils	800 kg.
Tallow or hardened fat	120
Rosin	80
Caustic soda, 27° Bé	ca. 850
Potassium carbonate solution, 30° Bé	130
Salt water 24° Bé	150
Waterglass 38° Bé ($Na_2O : 3SiO_2$)	54

The fats and broken-up rosin are melted together, added to the kettle with agitation, and the caustic soda and potassium carbonate solution, prewarmed to about 60°C., run with stirring into the melt, which has been brought to 75 to 80°C. When reaction has commenced, the salt water is added, followed by the waterglass previously mixed with lye. The soap is then transferred to the frames.

For colored soaps the dye solution is added to the frame and thoroughly stirred in. Now and then a small proportion of the tallow may be replaced by crude palm oil in order to give a more lively color.

FORMULA 2

Palm kernel oil or coconut oil	380 kg.
Tallow	250
Pale bone fat	100
Rosin	250
Caustic soda, 38° Bé	450

Potassium carbonate solution, 20° Bé	410
Salt water, 15° Bé	370
Waterglass, 38° Bé (Na_2O : $3SiO_2$)	237

The procedure is the same as with formula 1.

When using only fatty acids and rosin, the lye and filler are first brought into the kettle, then the fatty acids or the fatty acid rosin mixture. Typical mixes are given below:

White Soap with 220% Yield

1.	Palm kernel fatty acid or coconut fatty acid	300 kg.
	Tallow fatty acid	200
	Caustic soda, 30° Bé	360
	Waterglass, 38° Bé (Na_2O : $3SiO_2$)	140
	Salt water, 20° Bé	35

Pale Yellow Soap with 250% Yield

2.	Palm kernel fatty acids or coconut fatty acid	400 kg.
	Tallow fatty acid	100
	Rosin	100
	Caustic soda, 30° Bé	ca. 430
	Waterglass, 38° Bé (Na_2O : ca. $3SiO_2$)	150
	Salt water, 20° Bé	35

Lye and filler are introduced into the kettle and warmed to 80 to 90°C. The fatty acids or rosin–fatty acid mixture, brought to the same temperature, are added, and the whole mass well stirred until a homogeneously combined soap paste is in the kettle. This mass is left at rest for two hours before again stirring thoroughly several times. After testing for free alkali, the soap mass is transferred to the frames, where it solidifies.

Rosin or tall oil is very often used within the fat charge of semiboiled soaps. The following are some typical formulas for semiboiled soaps:

1. 365 parts palm kernel oil
   91.5 parts coconut oil
   64 parts rosin and/or tall oil
   265 parts caustic soda solution, 37° Bé
   180 parts waterglass (Na_2O : 3.22), 41° Bé ⎫ previously
   15 parts caustic soda solution, 36° Bé ⎭ prepared

2. 444 parts coconut and/or palm kernel oil
   222 parts light rosin
   333 parts caustic soda solution, 37° Bé

3. 100 parts coconut and/or palm kernel oil
   100 parts light rosin
   100 parts caustic soda solution, 37° Bé

It should be mentioned that it is possible to use the semiboiled process as the start for the production of the usual soap curd on lye or niger (see Chapter XII). As pointed out, an advantage of the semiboiled soap process over the cold process is that scrap is easily used up during the saponification process. The method is to dissolve the scrap in the kettle in some of the warm water used, with an addition of caustic lye, and then to add the saponification lye for the fat charge.

(5) Manufacture of Built Soaps

(A) DEFINITIONS

A genuine or pure soap contains 60 to 63% fatty acids when freshly pumped from the soap pan. Such a soap must be considered as the spontaneously formed product when a homogeneous soap solution is made to separate and settle into two phases: curd on clear lye, or neat soap on niger.

In some countries, specifications and standards exist that define very strictly the requirements such pure or genuine soaps must fulfill.

In trying to trace the interesting development the conception of *pure neat soap* had to undergo during the last forty years or so, we find the first country to work out and issue specifications and standards for the soap industry was Germany, as far as the European Continent is concerned. The German soapmakers' association issued the following standard specifications:

1910. Pure neat soap (*Kernseife*) is a product formed by the saponification of solid and liquid neutral fat and fatty acid with or withtout the addition of rosin, by one of the full-boiled processes, and by the subsequent graining of the soap from their solutions, by salt. It should contain at least 60% fatty acids.

1913. Neat soap is a product formed by the saponification of solid and liquid neutral fats and fatty acid, with or without the addition of rosin, with the condition that it contains at least 60% fatty acid when fresh. It should not contain added fillers or builders.

1925. As above, with the following remark: additions that do not reduce the fatty acid content of the soap below 60%, and are, in some way, helpful in building the detergent action of the product, should not be regarded as impurities.

It can be seen that there is a gradual relaxation from the strict definition of the term *neat soap* as presented in the various resolutions. In accordance with the first definition, it was indispensable to produce a settled neat soap to satisfy its terms, while the latter definitions had permitted the production of any unsettled soap provided that it contained at least 60% of fatty acid. Moreover, corresponding to the terms of the remark of the year 1925, it even became possible to add slight amounts of builders to the soaps and still call them pure neat soaps.

As an interesting example of the terms of certain definitions and standards undergoing decisive changes under the influence of changing economic and even political conditions, the adventure of the "neat soap" standards in

Germany before and after 1933 may again be cited. In 1925, the Reich committee for standard specifications again proposed to turn back to the first stricter definitions. In 1934, apparently under the impact of Germany's critical raw material position, the government not only relaxed the above specification, but actually ordered the production of soap containing no more than 52% of fatty acids, and gave permission to use the denomination *neat soap* for such a product if it contained not less than 50% of fatty acids.

We have already described the discussions that were being held in France in respect to the specification of neat soap. Standards for Marseilles soap prescribe that it should contain at least 72% anhydrous soap.

Under A. S. T. M. Designation D497-39, the following general requirements are mentioned for *ordinary bar soap*. It should be a well-made, uniformly mixed, bar soap, made from soda and fats, with no excessive proportions of rosin, and a moderate amount of matter insoluble in alcohol. Minimum content of anhydrous soap 52.0%; maximum moisture and volatile matter at 105°C. 36.0%; total matter insoluble in alcohol plus free alkali 2–10%.

The designation for built soap, powdered, D533-41, requires that it should be a high-grade product in powder form composed of soap and alkaline detergents. It should contain a minimum content of anhydrous soap of 50%; the sum of free alkali and total matter insoluble in alcohol 40% (max.).

The specification for milled soap, D455-39, requires a high-grade milled cake soap, as free as possible from water, thoroughly saponified; anhydrous soap content 83% (min.); sum of free alkali, total matter insoluble in alcohol, and sodium chloride, 1.7% (max.).

Not one of the specifications quoted, or any other existing to date, calls for a genuine soap in the strict significance of the term, as we had interpreted it in the sense of the phase rule. Even with milled toilet soap, there is a comparatively large margin allowed for added material. There is generally not more free alkali and salt than a maximum 0.7% in a milled soap. But even so there still remains a 1% margin for added materials insoluble in alcohol.

(B) The Merits of Soap Builders

In *A. S. T. M. Standards, 1946* (page 1015), the following definitions are given for the two terms, *filler* and *builder:*

Filler. A material added to soap or other detergent which does not improve its attractiveness or its effectiveness under the conditions of use.

Builder. A material added to soap or synthetic detergent to improve its effectiveness under the conditions of use.

There are still many soapmakers, especially in Europe, who are not familiar with the proper meaning of the two terms; and, in fact, in no other

language, except English, are these terms similar to those covered in English by *builder, building of soap,* or *built soap.*

In Germany, for instance, there is only one term in use which can be translated into English as "filling" or "extending." No wonder that the operation of "extending" the soap base composed of pure soap by adding materials of nonsoapy character to it was considered in Europe from an industrial and commercial viewpoint as something improper and even discreditable.

There is no discussion that, for instance, extending a cold-made coconut oil soap with salt and water is in fact an operation which must be regarded as an adulteration, should the product be sold with no special reference as to its true fat content. Everyone will agree that such a soap is of highly inferior quality as compared to an unfilled soap. But since it has been established by scientific test methods that combination between pure soap and certain alkaline salts give better detergent action than soap alone, it becomes obvious that "building of soap" (that is, combining pure soap with alkaline salts in proper proportions) has to be considered as a process improving the quality of the soap product.

Pure soap solutions as such develop an alkalinity corresponding to a *p*H value of 8.8–9.5, but it has been found that the best detergent action is displayed by soap solutions at a *p*H value of 10.7, and even values of over 11 have been mentioned (see Chapter XXX).

Alkaline salts (carbonates, silicates, borates, and phosphates, see Chapter IX) "build up" this required alkalinity which pure soaps in themselves are unable to attain in solutions.

Additional contributions of alkaline soap builders in such products are their softening action on the lime and magnesia salts present in ordinary water, also their action on certain metallic ions, and finally their help in keeping dirt suspended and fatty impurities emulsified in the detergent solution (see Chapter XXX).

Soap, when used alone, has to perform five functions in the laundry process: (*1*) to neutralize the acidity of the soiled washing, (*2*) to neutralize the acidity of the water used, (*3*) to neutralize the acidity of the fabric itself, (*4*) to precipitate the hardness of the water, and (*5*) to act as a detergent, that is, to emulsify and keep in suspension (peptization) the fatty and solid soil particles. In addition to all this, it must produce and keep up a certain optimal alkalinity, that is, pH 10.7–11.2, during the whole washing process.

According to Roshdestwensky,[24] 100 kg. of soiled washings contained 2 moles of acid and, for neutralization alone, needed soap calculated as 560 g. of fatty acids. (Snell[25] investigated the "break down" liquor in American

[24] D. Roshdestwensky, *Fettchem. Umschau, 40,* 237 (1933).
[25] F. D. Snell, *Soap,* No. 1, 29 (1932).

laundries and found 0.0105 mole acidity per liter, which would correspond, at a ratio of 1 : 4 between washings (load) and water, to 4.2 moles acidity per 100 kg. of load.) The 400 kg. of water used had a CO_2 acidity that had to be neutralized with soap equivalent to 150 g. of fatty acid, and finally the fabric itself adsorbed 300 g. of fatty acid as soap. Softening of the water used up (400 kg. water of 15° German hardness) 600 g. of fatty acid. The elimination of soil, that is, the washing process proper, is attained with 625 g. of fatty acid (always in terms of fatty acid in the form of soap).

Summing up the investigation, it may be stated that, of the total fatty acids used in his particular washing operation, 46% were used for neutralization of acidic material, 26% were used for softening of the water, and 28% were used for washing proper.

These figures make it more than obvious not only that washing with pure soap alone has to be considered as uneconomical and wasteful, but also that pure soap alone cannot produce the desired effects. It is curious that this fact was overlooked during a certain period, especially in European households. However, the reason may be found in the extreme lack of supply in fabrics of all kinds in Central Europe during and after World War I. So it may be understood that considerations concerning the preservation of fabric and prolongation of its life overrode every other consideration. The question of whether or not this was justified will be discussed later.

In any case, the American housewife and, to an even higher degree, the commercial launderer, never stopped the scientifically justified practice of using suitable amounts of alkaline electrolytes along with pure soap. These alkaline electrolytes (soda ash, trisodium phosphate, sodium silicate) are much cheaper than soap and are available in the United States from easily accessible raw materials. They are excellent for neutralizing, softening, and building up proper alkalinity, and aid soap in every respect in exercising its full detergent action.

It has been stated that by the use of such electrolytes in the various stages of the washing process, it was possible to bring down soap consumption in scientifically managed laundries in the United States to 0.8% fatty acids based on the weight of the fabric.

Experience with alkaline built soap powder fully bears out the evidence of the above considerations. It was proved experimentally that with 1 kg. of a soap powder combination containing 400 g. of fatty acids (equivalent to 700 g. of neat soap) and 400 g. of sodium carbonate it is possible to wash two and a half times more soiled washings than with the soap alone.

Only a few of the exact experiments which confirmed the above statement during the last 15 years need be cited here. Rhodes and Bascom[26] found that the detergency of 0.25% soap solution increases with alkali addition up

[26] F. H. Rhodes and C. H. Bascom, *Ind. Eng. Chem., 23,* 778 (1931).

to a pH value of 10.7, and that the action of the builder is proportional to the valency of its anion.

Baker[27] demonstrated in actual laundry experiments that the higher the pH of the liquor, the smaller the amount of soap necessary to effect the same result. Table XIX-6 shows these results.

The relation between the required amounts of alkaline salt of different kinds and the pH of the liquors thereby obtained in actual laundry practice is shown in Chapter XXX. The corresponding data were derived from actual titrations of the liquor in experiments conducted in a Chicago laundry.

The evidence given above sufficiently bears out the justification of the use of alkaline builders in soap powders and solid soaps. The practical sense of the American consumer made possible the introduction of reasonably built soaps as market brands which were sufficiently inexpensive and at the same time rational in use and highly efficient. That is also the reason why the A. S. T. M. standards, unlike other specifications (which, in the opinion of

TABLE XIX-6

SOAP CONSUMPTION AT VARYING pH VALUES OF THE LIQUOR[27]

pH of liquor	9.9	10.8	11.3
Soap used for 408 kg. of washing, kg.	5.18	3.29	2.74

the authors, must now be considered somewhat out of date), do not find it necessary to define the genuine pure soaps as a product in the sense of the phase rule and, for the most items, leave ample margin for the use of alkaline builders in the soap product.

(C) EFFECT OF ALKALINE BUILDERS ON FABRIC

As already mentioned, there was, however, at the beginning, a serious objection in the mind of the consuming public against the use of alkaline built soap products. There has been, in the last 30 years, a considerable controversy concerning the alleged destructive action of alkaline solutions on the various fabrics. This, in fact, was one of the problems that had to be settled before soapmakers and public could make up their minds as to whether or not to accept alkaline built soaps as equivalent detergents able to compete with pure soap in every respect.

A discussion of some of the investigations carried out in this direction should be of interest. Such investigations were carried out in Central Europe on a wide scale, due probably to the fact mentioned above that in these countries special circumstances rendered the necessity of fabric conservation a matter of first priority.

[27] C. L. Baker, *Ind. Eng. Chem.*, 23, 1025 (1931).

The launderers' association of Switzerland carried out laundry experiments of very wide scope under the supervision of A. Haeuptly[28] of St. Gallen, as summed up in Table XIX-7. Cotton fabric was washed in various detergent combinations 80 times, and tested for tear resistance and breaking strength in both directions. The results of these experiments clearly bear out that it is, in the first place, the oxidative bleaching which greatly reduces the lifetime of the fabrics. On the other hand, combinations of pure soap with soda ash are somewhat more harmful than soap alone; but last and most important, when sodium silicate is added to the combination, the mixture resulting has better preserving properties than soap alone.

There are some more recent investigations by Roshdestwensky[29] concerning the effect of soda ash on fabrics. Soda will be absorbed by fabrics in

TABLE XIX-7

FIBER STRENGTH CONSERVATION BY VARIOUS DETERGENT MIXTURES[28]

No.	Detergent	Warp		Woof	
		R^a	B^b	R^a	B^b
1	Pure soap	62.7	83.8	51.3	174.1
2	" plus soda ash	52.1	92.6	49.5	81.9
3	" " " " plus sodium silicate	75.1	101.5	71.2	129.3
4	" " " " plus sodium perborate	40.5	83.8	40.0	98.3
5	Persil (alk. soap powder containing soap plus Na$_2$CO$_3$ plus Na$_2$SO$_3$ plus perborate)	31.5	72.1	26.6	82.7
6	Soap plus soda plus ozone when rinsing	62.6	77.3	55.9	134.5
7	" " " plus bleaching with hypochlorite	38.8	86.8	37.4	98.3
8	Soap plus soda plus bleaching with H$_2$O$_2$	44.4	79.4	41.1	91.4

[a] R, tear resistance.
[b] B, breaking strength.

proportion to the strength of the solution used. Soda crystals are deposited in the cavities existing in the fibers and thereby produce a destructive effect, which makes itself felt in practice only when the concentration of the soda solution is in excess of 0.25%. In concentrations of 0.1 to 0.2% these effects do not materialize. Fabric washed 30 times with a solution mixture containing soap and soda in 1 : 1 proportion reduced the fiber strength only by 18%, while in a proportion of 1 : 2, 25% of strength was lost.

(D) TECHNICAL ASPECTS OF BAR SOAP BUILDING

It is not as easy as it may seem to combine a liquid soap with builders. The difficulties described below were probably not felt as keenly in the United States as in Europe. This is due to the fact that in the United States the pro-

[28] A. Haeuptly, Communication of the Swiss Federal Launderers Association, St. Gallen, Switzerland.

[29] D. Roshdestwensky, *Masloboino-Zhirovoe Delo;* through *Fette u. Seifen,* 1938, p. 325.

duction of built-up soaps was always considered as the customary course of the manufacturing process. In fact, it can be said that in the United States neat soap is regarded in most factories as an intermediary product serving only as a basis for the subsequent production of built-up soap. This is, at least, the case in the manufacture of the ordinary brands of household soaps. Equipment in the American soap factories was adopted from the outset for this purpose, and there were no particular difficulties encountered, at least in the mechanical sense. However, no soapmaker would deny that from a chemical point of view great care has to be taken to overcome incompatibilities in certain cases between a particular neat soap base and the liquor prepared for building up the soap.

The mechanical devices lacking in Central Europe at the time the building of bar soap was reintroduced (1933) were especially suitable crutchers and frames. Soap manufacturers there had mostly stopped using the time-honored cooling methods in forms or frames. They had been applying for some time the more modern procedure of cooling in machines, where the liquid soap mass is cooled down in a matter of one to two hours to a solid slab of suitable thickness. Such a slab requires afterward only the customary cutting table for cutting into cakes.

The pros and cons of the modern method as opposed to the old method are fully discussed, together with the problems of the apparatus, in Chapter XXIII, Section 3. Here, we merely mention that European manufacturers found it particularly difficult to produce built bar soaps because a built soap when produced with large amounts of silicate or soda and reduced to a fatty acid content well below about 55% becomes a viscous mass which is difficult to handle without the use of suitable crutchers and difficult to introduce into cooling presses.

A great deal of discussion has taken place in this respect during the last few decades and, as a result, the building of soap became a scientifically better controlled procedure than ever before.

A properly built soap, and accordingly the base soap to be treated and the liquor composed for building, should satisfy the following set of requirements. (a) The fat charge should have a L.L.C. sufficiently high to withstand the graining effect of the building liquor. (b) The fat charge should furnish soap of such plasticity as would counterbalance the hardening effect of the builder. (c) The neat soap should be sufficiently settled and free of electrolytes so that it will not interfere with the effect of the calculated amount of electrolytes added. (d) It should have sufficient alkali to withstand the neutralizing effect when acid sodium silicate is added. (e) The electrolyte solution or mixture should be of the proper strength in order to fit the L.L.C. of the soap base and not interfere with the homogeneity of the phase. (f) In addition to sodium silicate it should contain such salts or alkalies as

are able to thin out the mass and make it more suitable for handling in the crutcher and for charging into frames or cooling presses. (g) The built soap should present a homogeneous, firm, but not brittle, cake or bar which keeps its homogeneity for an unlimited period without producing any precipitate on its surface or separating any liquor.

It is known that soap is more sensitive to the graining action of a certain electrolyte concentration in the cold than at higher temperatures. This is why the building liquor should be reduced to a concentration at which the soap is able to preserve its homogeneity, even at the lowest temperature to which it may be exposed. When this condition is fulfilled, there will be less danger of any liquor separating subsequently.

A soap treated like this would, on the other hand, be better preserved against rapid drying out. There are conditions acting as a kind of vicious circle; when electrolytes concentrate in the soap as a result of evaporation of water from the soap cake, this may cause partial graining and more separation of water at the surface, which would, in turn, evaporate, and so on.

With the use of carbonate, there is more danger than with any other electrolyte that white precipitates may appear on the surface. Chlorides are very strong in their graining action. NaCl should be used in addition to other electrolytes when these show a tendency to soften the soap. NaCl solutions should never be used alone for the building of soap, but always together with sodium silicate. Sodium silicate is the only builder which, when used reasonably, does not precipitate on the surface in the form of a white layer. It is assumed that sodium silicate forms a kind of crust on the surface which closes its pores against the tendency of the electrolytes to pass through it.

A dilemma arose with the use of neutral sodium silicate when it was experienced that such an addition made the mass so viscous as to render handling impossible, except in very strong crutchers; cooling in machines was likewise not feasible. The alternative was to use more caustic alkali than required for neutralization of the free silicon dioxide, or to use some other salts along with the builder for somewhat softening the mass. In the former case, however, the soap became alkaline, and in the latter, there was the danger of *bloom*. The neutralization of sodium silicate $1Na_2O : 3SiO_2$ (38° Bé) with dry sodium carbonate is reported to give a mixture of excellent properties as a builder, and it has been stated that it shows no tendency to produce white bloom.

It has been pointed out by one author that the presence of rosin in the charge preserves built soap against bloom. The same author mentions, incidentally, that sodium sulfate, when added to sodium silicate, counteracts the thickening effect of the latter, thus making possible the use of cooling presses for silicate built soaps.

As a matter of interest, it should be mentioned that other means for thinning out soaps built with silicate solution were proposed. These are: small additions of sugar solutions or the use of a small quantity of citronellol.

(E) PHYSICAL NATURE OF BUILT SOAPS

The physical nature of practical soap systems containing added salt solutions was not investigated, and it was only recently that Wigner[30] outlined some interesting considerations which may be applied to control more precisely the process of soap building. According to Wigner's explanation, there are four main groups of built bar soaps. (1) Soaps, liquored with salt solutions containing down to 60% fatty acid. (2) Run soaps containing 40–50% fatty acids. (3) Glued-up soaps with normally 56–58%, but sometimes lower, fatty acid content. (4) Run soaps containing less than 40% fatty acid.

Each of these classes represents a different type of physical state, and their manufacture can be facilitated greatly when this had been sufficiently understood. Let us examine each group individually.

(1) These are essentially identical with pure settled neat soaps. They always represent one homogeneous phase. It was seen on the phase diagram that neat soap is able to exist throughout a whole range of compositions containing from 60 up to 63% of fatty acids, and also varying percentages of salt. Table V-7, reproduced from Wigner's work, shows such a range of neat soap compositions. It was also shown (see Ch. V, 2) that neat soap resulting from a rough fit containing, say, 63% of fatty acid, and a certain quantity of salt, can be transformed into neat soap containing only 60% fatty acid, and a quantity of salt corresponding to this point in the phase diagram. This is accomplished by the addition of salt solutions of suitable concentration. How this should be done by using Table V-7 or the diagram containing the plotting of the figures from Fig. V-1 was discussed earlier.

In Fig. V-1, fatty acid content is plotted against salt content in the free solution. For the use of his method in the production of liquored soaps, Wigner advises plotting fatty acid content against salt content in the neat soap. From such a chart it is easy to extrapolate any fatty acid value and the corresponding content of salt which such a soap should contain when in real equilibrium. It is then an easy matter to calculate the quantity of water and the quantity of salt required for the dilution of the concentrated soaps to the less concentrated ones. But, since the water and salt quantities required for the operation are known, the concentrations of the salt solution to be used are known as well.

Let us consider a concrete example. By extrapolation from Fig. V-1

[30] J. H. Wigner, *Soap Manufacture. The Chemical Process*, Chemical Pub. Co., New York, 1940.

(which was drawn by using values found for fatty acid versus salt content in varying experimental fittings), we know that with a certain fat charge a neat soap contains 0.434% NaCl with 63% fatty acids, and 0.632% NaCl with 60% fatty acids. In order to prepare a 60% soap from a 63% soap, we have to increase the weight of 100 g. soap to 105 g. This 105 g. of soap should contain $105 \times 0.632/100 = 0.664$ g. of salt, which means that we must add $0.664 - 0.434 = 0.230$ g. salt, or 5 g. solution containing 0.230 g. salt. The solution to be added must consequently contain $(100 \times 0.230)/5 = 4.6\%$ salt.

For each type of fat charge the basic figures and charts must be established by small-scale boils and by the determination of fatty acid and salt content in the separated neat soap. Series of fittings with varying amounts of salt in the free solution must be made and investigated. By using these figures and charts derived from them, it becomes possible to transform any rough fit into the corresponding fine fit containing less fatty acid.

It must be stated that when the transformed soap is made to contain more electrolyte than it could according to the chart, the new soap would not be a homogeneous phase, and it would tend to separate some liquor. When, on the other hand, the liquored soap contains less salt than it should, according to the chart, then the consistency would be too soft.

(2) The soaps belonging to this class also represent one homogeneous phase just as the liquored soaps dealt with under (1). Because of the low fatty acid contents between 30 and 40%, these soaps belong to the phase diagram of the area of the niger. The salt contents of these soaps must therefore be adjusted in such a way that for any fatty acid content the corresponding electrolyte content of the particular niger is strictly correlated.

The properties and composition of nigers can be studied by small-scale experiments. Here, again, fatty acid contents can be plotted against salt contents in the niger. Thus, theoretically, any type of niger can be prepared by suitable addition of salt solution to a neat or curd soap. It is known, of course, that ordinary nigers of low concentration are quite soft and would be unsuitable for use as bar soaps. However, it makes a difference when sodium carbonate is used instead of salt and when the fat charge contains fats which produce sufficiently hard soaps. The amount of sodium silicate equivalent to the required quantity of salt as established may be calculated when each part of Na_2O present in the sodium silicate is taken as 1.3 parts of NaCl.

Let us again take an example from Table V-7. From the chart in Fig. V-1 we can determine that a 28% fatty acid niger contains a free solution of 8.8% salt concentration, and a niger with 40% of fatty acids contains a free solution with 7.2% salt. From this, the absolute amount of salt contained in these nigers can be calculated in the following manner. The 28% niger contains $28 \times 1.52 = 42.5\%$ of 66% soap hydrate and $100 - 42.5 = 57.5\%$ free solution, or $(57.5 \times 8.8)/100 = 5.0\%$ of salt in the niger. In the

same manner it can be calculated that the 40% niger contains 2.8% of salt.

The 63% neat soap contains 0.434% salt. In order to have a 28% solution, we dilute 100 g. to 225 g., and add 125 g. of solution. This 225 g. must contain, however, $(225 \times 5.0)/100 = 12.25$ g. of salt. We add $11.25 - 0.43 = 10.82$ g. of salt in 125 g. solution, or a solution of 8.7%.

To recalculate this amount of salt solution into a sodium silicate solution: 3 parts of alkaline sodium silicate contains roughly 1 part of Na_2O; 3 parts of this silicate is equivalent to 1.3 parts of salt. 10.82 g. of salt is equivalent to $1.3 : 3 = 10.82 : x$; $x = 25.0$ g. of sodium silicate $(2 : 1)$, that is, the strength of the silicate solution is $(25.0 \times 100)/125 = 20\%$.

In order to obtain the 40% niger we dilute the 100 g. of 63% neat to 157 g. of total weight. This 157 g. of niger must contain $(157 \times 2.8/100 = 4.4$ g. of salt. 3.97 g. salt is equivalent to 9.1 g. of sodium silicate $(2 : 1)$. Consequently, we add 57 g. of a 16% sodium silicate solution to 100 g. of neat soap (about 17° Bé).

However, what has been explained before with respect to the difference between the susceptibility of electrolytes of soaps in the hot and cooled states must be kept in mind. The above calculation has only approximate validity, since in actual practice the silicate concentration is somewhat too high.

In fact, all practical soapmakers recommend laboratory trials before deciding what concentration a solution should have for a successful running.

Wigner advises that these trial runnings be carried out by making, with each fat charge, a series of runnings with varying silicate of soda concentrations, taking samples from the crutcher and setting them aside in beakers. When the running produces the proper quality of trial soap, the contents of the beaker are separated into two layers; but, in such cases, the upper layer is very small in proportion. When the silicate solution is too strong, the upper layer is too large and the ready soap is rough in texture and probably also separates liquor to some extent. When too weak a silicate solution is used, there is no upper layer at all and the ready soap is then too soft. In such a way, tabulated data can be worked out for each kind of fat charge, in which the degree of running (that is, the fatty acid content of the running soap) is correlated to the sodium silicate lye concentration which proved to be suitable throughout the trial runs.

(3) Such soaps do not consist of a homogeneous phase. They are, rather, an emulsion of neat soap and niger in suitable proportions, and it is apparently the silicate of soda which acts as an emulsifier between the two phases present. There is certainly a tendency for separation in this heterogeneous system, and, in order to obtain a properly uniform product, the mixture must be agitated until low temperatures are reached, and run into the frames only after the risk of separation has been eliminated completely.

According to Wigner, the best final products of this type were produced when the corresponding trial tests separated into two layers, the upper of which consisted of about 35% of the total mass. In such cases the upper layer contained about 60–61% of fatty acids. The concentration of the silicate lye which causes this particular degree of separation must be found experimentally.

(4) These soaps are emulsions of neat soaps and of soap dissolved in a strong solution of silicate and carbonate. Glued-up soaps are made with strong solution of silicate or carbonate of soda. This soap becomes very viscous in the crutcher and cannot be run into the frame on account of its consistency. The fat charge contains solid fats of the tallow and palm oil class and also considerable quantities of rosin.
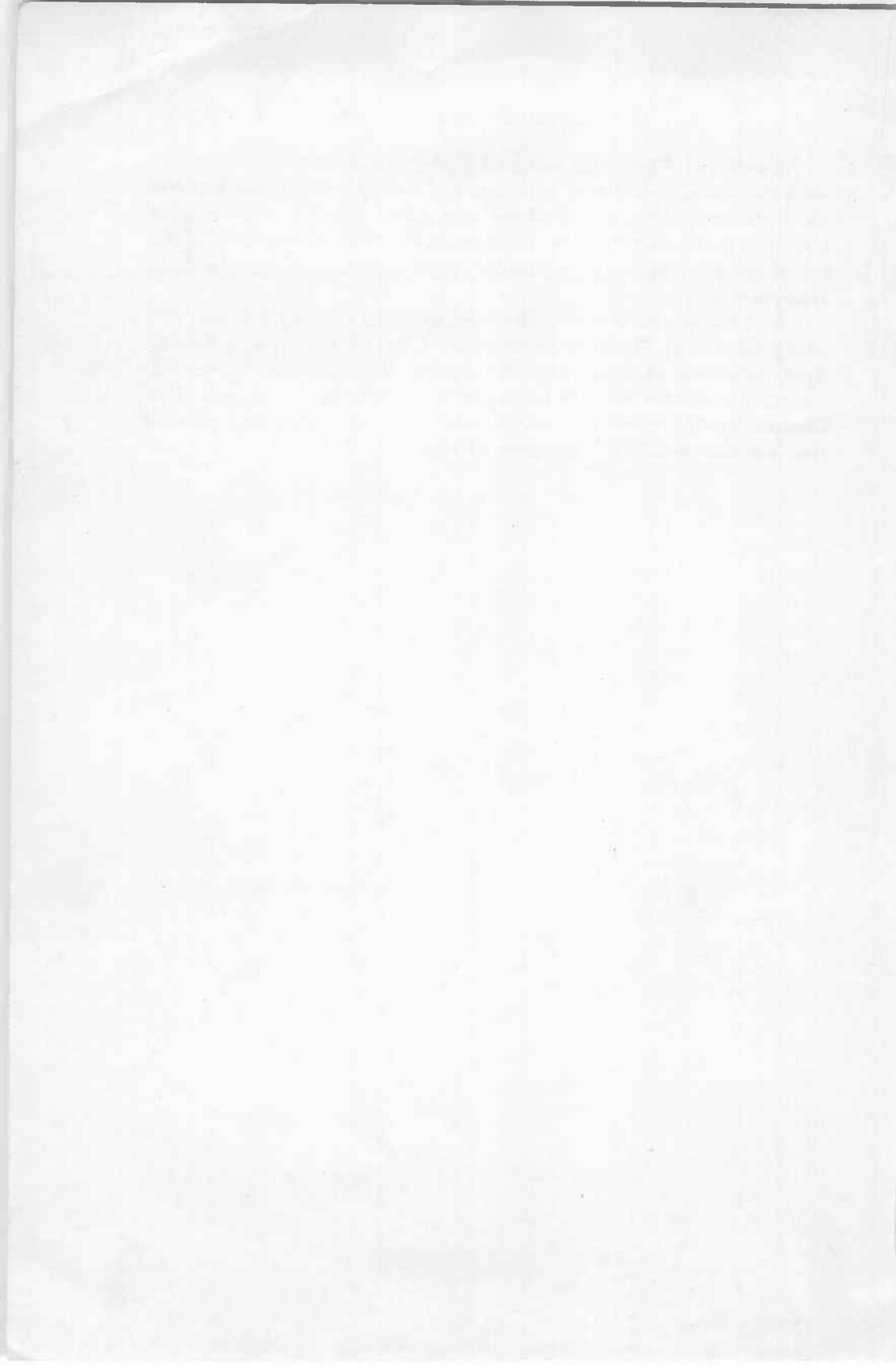
PART D

Special Soap Products
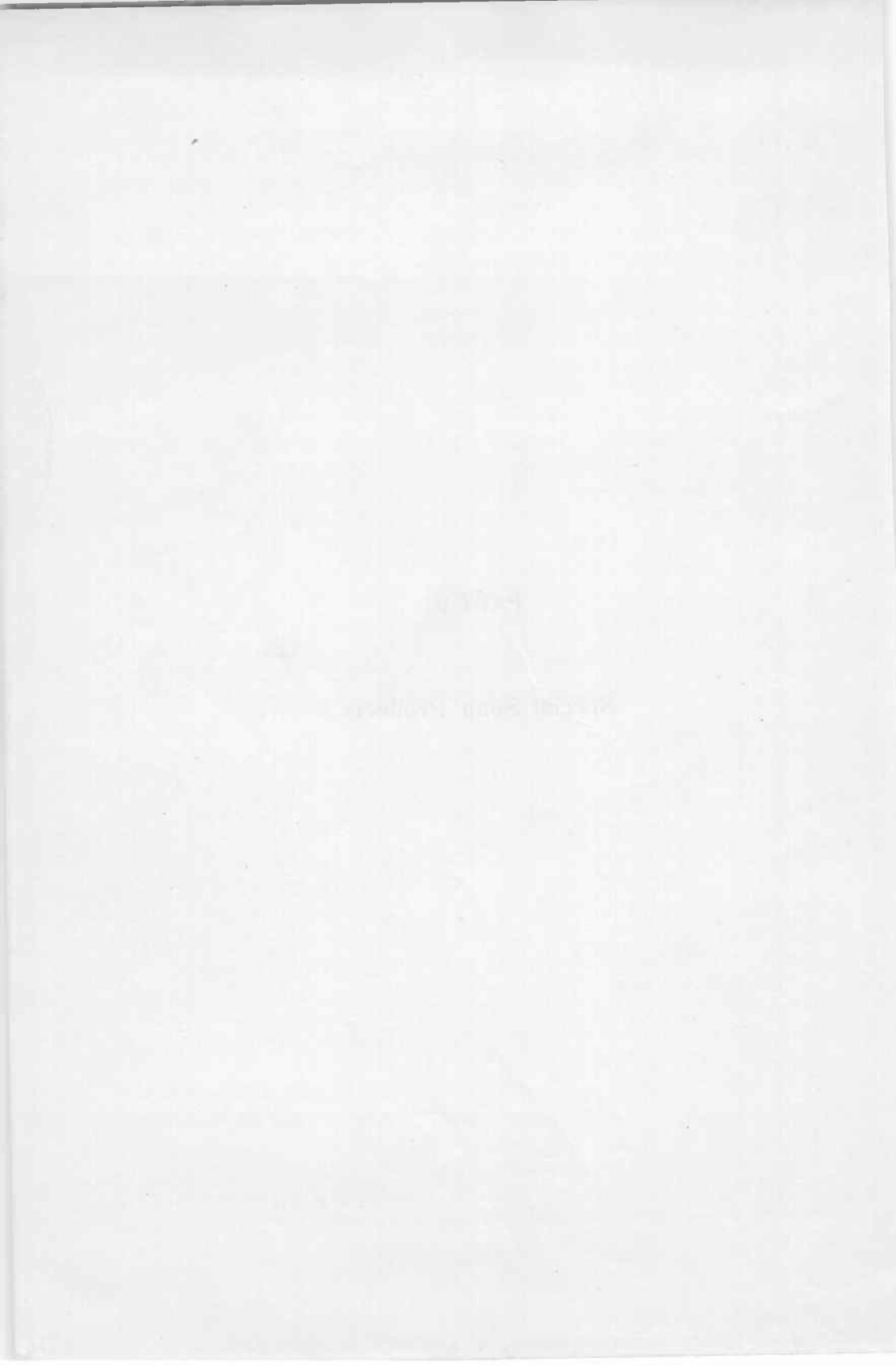
TECHNICAL SOAPS

(1) Solvent and Dry Cleaning Soaps

(A) Solvent Soaps

Solvent soaps are finding application in the textile industry as well as in the laundering trade. Normally, they contain only 5–15% solvent, inclusive of the emulsifying agents when the latter have solvent properties. This small percentage of solvent does not exercise a dissolving action in the literal sense of the word. but rather reinforces the ordinary detergent action of the soap. Considering, for example, that in using 0.5% of a solvent soap containing 10% solvent in 100 liters of wash liquor not more than 50 g. of solvent is present, it is evident that the solvents incorporated within the soap cannot function as "solvents" in the ordinary sense. Their function is rather to intensify the *solubilization* effect of the soap itself upon the fat and dirt in the treated material. More recent research on the solubilization effect of soap (Chap. XXX, 4, F), however, may prove that the value of even small percentages of solvents in the soap may be greater than anticipated in earlier publications.

It would be a mistake to assume the incorporation of a solvent in a soap to be invariably a straightforward matter. It is a question not merely of firmly anchoring the solvent in the soap—and even this is not so easy when larger proportions of solvent are to be employed—but also of securing fine distribution of the solvent and the soap in the wash liquor during actual washing procedures so as to enable the solvent to reinforce the detergent ac-

tion of the soap instead of rising immediately to the surface in the form of practically unemulsified droplets. Solvents are maintained in distribution within the soap with the aid of emulsifiers. Turkey red oils may be recommended for this purpose. Mixtures of 1 : 1 to 1 : 2 parts of highly concentrated turkey red oil with solvents are quite easy to incorporate into soap. The solubility of highly concentrated turkey red oil was the subject of a paper by A. Davidsohn.[1a] Many other emulsifying agents are, of course, now available.

If aliphatic petroleum is used in solvent soaps it is customary to limit the amount to about 10 parts of petroleum per 100 parts of finished soap. Both petroleum soft soaps and petroleum bar soaps are known. In small percentages the petroleum is simply incorporated with the soap paste.

Incorporation of 6–10% solvent presents no special difficulties, but it is always advisable to include 3–4% (calculated on the soap) of emulsifiers, because a good distribution of solvent in the soap and in the processing bath is then ensured. Solvents of the most diverse character are suitable in general for such products. Especially effective are oil of turpentine and related substances, the higher boiling hydrocarbons, chlorinated hydrocarbons, etc. Preparation follows exactly the same lines as for petroleum soaps. Emulsifiers are indispensable in most cases.

A high percentage of tall oil in the fat charge promotes the incorporation of solvents. On the other hand, a high percentage of coconut oil or palm kernel oil (or their fatty acids) in the fat charge makes the incorporation of solvents more difficult. This is in accordance with results obtained by exact physico-chemical investigation on the solubilization of water insoluble hydrocarbons by solutions of soaps from fatty acids of varying molecular weight.[1b] With regard to the ease of solubilization of different types of solvents, the following generalizations can be made: polar solvents are more readily solubilized than non-polar solvents, aromatic compounds more than aliphatic, and branched chains more than straight.

Some modern solvents are, in a sense, emulsifying agents themselves, e.g., the hydrogenated solvents: cyclohexanol (hydrogenated phenol) and methylcyclohexanol (hydrogenated cresol), both of which possess high solvent power for fats, oils, waxes, resins, dyes, mineral oils, highly oxidized fats, rubber, metallic salts of fatty and resin acids, and the like. They are miscible in all proportions with benzol, tetralin, decalin, oil of turpentine, chlorinated hydrocarbons, etc. The hydrogenated phenols are more readily dispersed in water because they possess free hydroxyl groups. In combination with ordinary soaps, cyclohexanol and methylcyclohexanol develop ef-

[1a] A. Davidsohn, J. Am. Oil Chem. Soc., 28, 84, 85 (1951).

[1b] J. W. McBain and K. E. Johnson, J. Am. Chem. Soc., 66, 9 (1944).

fects similar to those of turkey red oils by increasing the lime resistance of soap. Cyclohexanol soaps are therefore products that can be successfully applied in the textile industries and in laundries as spotting agents and dry cleaning soaps. They are of far greater importance than the petroleum soaps.

Several formulas are now given to illustrate the ease with which liquid or soft paste type cyclohexanol or methylcyclohexanol soaps can be prepared with the most diverse fatty acids which at the same time fulfil all technical requirements:

(1) Linseed oil	500 kg.
Cyclohexanol	200–300
Caustic potash (50° Bé)	199
Water	1208
(2) Linseed oil fatty acid	500 kg.
Methylcyclohexanol	750
Caustic potash (50° Bé)	208
Water	292
(3) Linseed oil	500 kg.
Methylcyclohexanol	300
Caustic potash (50° Bé)	100
Caustic soda (36° Bé)	120
Water	230

The ingredients of each batch are stirred together in a kettle heated by indirect steam until a clear solution and clear solubility in water are attained, after which the mass is tested for alkalinity.

As already pointed out, the hydrogenated phenols promote the union of fats and aqueous alkali by this method and thereby accelerate the reaction.[1]

It is also permissible to use finished soap as a starting base. A textile preparation is thus obtained by adding 10.5 parts cyclohexanol to a solution of 10 parts of Marseilles soap in 200 parts of water.

Preparations made along the lines of the foregoing formulas possess good lathering power, although this is reduced on adding abnormally large proportions of cyclohexanol or methylcyclohexanol.

Homogeneous water-soluble preparations are also obtainable when using other solvents such as benzene, benzol, carbon tetrachloride, tetralin, etc. in combination with cyclohexanol and methylcyclohexanol. Two examples of satisfactory compositions are:

(1) Linseed oil	184 kg.
Cyclohexanol	275
Caustic potash (50° Bé)	73.5
Water	387
Carbon tetrachloride	80

[1] See *Seifenindustrie-Kalender*, Berlin, 1927, p. 90. A. Davidsohn, *Les Matières grasses*, Nos. 360 and 361 (1938).

(2) Coconut oil	51 kg.
Linseed oil	42
Cyclohexanol	130
Caustic potash (50° Bé)	42
Water	615
Carbon tetrachloride	120

In the above formulas, the place of carbon tetrachloride may be taken by benzene and higher boiling fractions of petroleum in approximately the same proportion. It must be mentioned that those hydrogenated aromatic solvents are very effective in improving the lime stability of a soap. By replacing the fats and oils in these formulas by their corresponding fatty acids the manufacturing process may be considerably simplified. The fatty acids are dissolved in the solvents and added to the alkali–water solution with stirring at about 60°C.

Another important solvent emulsifier is trimethylcyclohexanol. Less important but still very useful for solvent soaps are tetrahydronaphthalene (tetralin) and decahydronaphthalene (decalin), both, as the names imply, being hydrogenated naphthalene derivatives. It must be mentioned that pine oil too, owing to its content of free hydroxyl groups, acts as a kind of combined solvent–emulsifier.

Other solvent emulsifiers are the solvents of the Carbitol and Cellosolve types (see Table XX-1) and the so-called Carbowaxes (polyethylene glycols). As a matter of fact, emulsifiers of the sulfonate type built up on more complex structure than simple turkey red oil are valuable auxiliaries for the production of solvent soaps as well. There are so many emulsifying agents of this type on the market, that it is impossible here to select at random a few from a list of hundreds.[2]

Very interesting observations about "blending soaps with organic solvents" were published by Palit:[3]

It has been observed[a] that soaps, the alkali metal salts of long fatty acids, are highly soluble in a mixture of solvents, termed G–H mixtures. Here G stands for any glycol or any dihydroxylic solvent, particularly with the two hydroxyl groups in contiguous position, and H stands for any hydrocarbon or a solvent which can dissolve hydrocarbon, for example, chlorinated hydrocarbons, alcohols, ketones, etc. The mixed solvent has a high solvent power for soap even when the separate solvents do not dissolve it. We shall call this enhanced dissolving power of a mixture "co-solvency" and the individual solvents co-solvents. In cases where one of the co-solvents is a fairly good solvent and the other is practically a nonsolvent in the pure state we might call the latter a latent solvent or an activator, particularly if it is required in a comparatively small proportion to produce a large effect.

Ordinary soaps can be dissolved in hydrocarbons by the use of glycol type com-

2 *Soap & Sanit. Chem.*, Aug., Sept., Oct. (1949).
3 S. R. Palit, *Soap, Perfumery and Cosmetics, 19,* 471 (1946).
4 S. R. Palit, *J. Indian Chem. Soc., 19,* 271 (1942).

pounds as co-solvents. Unfortunately, however, ordinary glycols are immiscible with hydrocarbons, and hence higher glycols or other derivatives which are fairly miscible with hydrocarbons must often be sought. In compounding such mixtures, the now well-known property of soap of bringing about a pronounced increase in the mutual solubility of liquids will be of help. This is particularly true as the author has observed that soaps profoundly increase the mutual solubility of a glycol and a hydrocarbon. For example, an addition of 15% sodium oleate will make benzene and propylene glycol, completely miscible at room temperature, forming a clear mobile fluid, although the critical solution temperature of the system without soap is near 80°C. If a few of the paraffinic hydrogen atoms in glycol could be replaced by large alkyl or aryl radicals, the resulting compounds might be expected to serve our purpose. In the absence of commercial availability of such compounds, dibutyl tartrate and diamyl tartrate, sold as nitrocellulose plasticizers, bid fair to satisfy the needs, since besides the two contiguous hydroxyl groups as in a glycol, they are miscible with hydrocarbons like benzene, cyclohexane, hexane, etc., due evidently to the presence of the COOR groups. Besides acting as expected from our theory as a powerful solvent and co-solvent for soap, these compounds have one very desirable property which makes them almost ideal for our purpose. These solvents have very little tendency to gel soaps, so that if a solution of a soap in hydrocarbon–dibutyl tartrate mixture is cooled, jellies are not formed, but the dissolved soap precipitates, usually in the crystalline state.

The solubility of soap in dibutyl tartrate is very high, and it is greatly increased by the presence of small proportions of hydrocarbons or chlorinated hydrocarbons. Thus, 100 g. of dibutyl tartrate dissolves 41.3 g. of sodium oleate at 25°C. and an addition of about 20% of chloroform, benzene, amyl alcohol or any H-solvent increases the solubility by 10 to 30%. A very useful property of such solutions is that they can be diluted with light petroleum fractions without precipitation of the soap. Hence, to prepare oil soluble commercial soap, particularly castile soap, is dissolved in dibutyl tartrate containing 20% benzene or trichloroethylene. In this way, a 30% solution of soap is easily prepared.

The same stock solution of soap can be used for dry cleaning, since this stock solution can be diluted by dry cleaning fluids, like Stoddard solvent, without precipitation of soap. Such solutions have been found to have good detergent power.

The use of combinations of synthetic detergents with solvents has recently found entry in many fields of industry.[4a] Many non-ionic detergents strongly promote the formation of stable one-phase structures of solvents with soaps or anionic detergents. The use of addition of non-ionic detergents is recommended in cases where difficulties in incorporating solvents into soaps arise.

(B) DRY CLEANING SOAPS

A special kind of solvent soap are the dry cleaning soaps, which act as detergents, not in aqueous solution, but in the solvent used for dry cleaning.

Ordinary solvent soaps cannot be used for dry cleaning because they are not soluble in the solvents commonly used for this purpose, and it is therefore necessary to produce a soap which is soluble, or at least dispersible, in cleaning naphthas. The solubility of the soap body is generally attained by leaving a large excess of fatty acids, and producing an *acid soap*. Used as saponifying agents are caustic soda, caustic potash, sodium carbonate, potas-

[4a] A. Davidsohn, *Soap, Perfumery and Cosmetics, 25,* 724 (1952).

sium carbonate, ammonia, and organic bases such as triethanolamine. Small amounts of alkaline earth salts, such as $MgCO_3$, are sometimes used to form soaps having antistatic properties.

The manufacture of dry cleaning soaps consists of heating the fatty acids (neutral fats are seldom used) with the solvent or solvent mixture in a suitable vessel, and adding the saponifying agents, stirring well, and taking care to leave an excess of fatty acids. Depending on the composition, dry cleaning soap may be liquid or of pasty consistency; solid dry cleaning soaps are rare, containing, as they do, little solvent, and are therefore less soluble in the solvent.

The following examples demonstrate the composition of a number of dry cleaning soaps:

A. 35.0 parts oleic acid
    8.0 parts stearin
    7.0 parts caustic potash (calc. as 100%)
    0.5 parts ammonia solution (25%)
    10.0 parts water
    40.0 parts benzene

The mode of preparation is as follows:

The stearic acid is dissolved in the oleic acid and the benzene added and heated to near boiling point of the solvent. To it is added the caustic potash dissolved in the water, with careful stirring. Finally, the ammonia is added.

B. 20.0 parts soft soap
    2.0 parts oleic acid

are dissolved in:

    40.0 parts water
    10.0 parts alcohol

To this solution is added:

    20.0 parts tetrachloroethane or trichloroethylene.

(This soap is suitable for chlorinated hydrocarbon solvents.)

C. 50.0 parts oleic acid
    40.0 parts alcohol

are dissolved and carefully mixed at 60°C. with 6–7 parts of a 25% ammonia solution.

This soap can be dissolved in a suitable solvent, as, for example, cyclohexanol, which renders it more easily soluble in Stoddard solvent, etc., although it can also be marketed without the solvent.

D. 100 parts oleic acid
    100 parts butyl Cellosolve
    25 parts cleaner's naphtha

are heated to 60°C. To this solution is added a mixture of 20.5 parts of triethanolamine, 8 parts of caustic potash (calc. as 100%), and 13 parts of water.

E–F. Further formulas for dry cleaning soaps are:[5]

[5] *Emulsions,* 7th ed., Carbide and Carbon Chemicals Corporation, New York, 1946, pp. 66–68.

Constituent	Per cent of oleic acid saponified	
	80%	90%
Oleic acid	107 lb.	107 lb.
Cleaner's naphtha	25	25
Butyl Cellosolve	27	27
Triethanolamine	21	—
Monoethanolamine	—	10.5
Potassium hydroxide (100% basis)	8.3	9.5
Water	13.5	13.5

1. Heat the oleic acid, butyl Cellosolve, and naphtha to 140°F. Avoid an open flame.

2. In a separate container, dissolve the potassium hydroxide in the water and add the amine.

3. Then stir the water solution into the oleic acid solution.

4. Continue stirring for about 30 minutes to permit all of the potassium hydroxide to react. The solution should be clear.

Mixed isopropanolamine may be used to replace triethanolamine in these formulas to produce greater oil solubility.

These soaps are soluble in naphtha in all proportions and, being more completely saponified than the usual dry cleaning soap, they are more concentrated and less is needed in the solvent. Butyl Cellosolve is a particularly effective coupling agent for dry cleaning soaps and allows the addition of water, a necessity for good detergent action. It also assists in removing food stains and other water-soluble spots, and aids in brightening the colors of the garments being cleaned. In fact, one important function of a dry cleaning soap is to absorb the moisture from the textile surface and permit inimate solvent contact, as discussed below. Here is another formula:

G.	Butyl Cellosolve	25 lbs.
	Oleic acid	95
	Stearic acid	12
	Triethanolamine	19.7
	Potassium hydroxide	8.3
	Water	10

This dry cleaning soap is a thin paste and is suggested as a scrubbing and spotting soap. A more viscous paste may be obtained by increasing the stearic acid content and decreasing the oleic acid content by the same amount. The soap is completely soluble in naphtha.

Soaps boiled on similar principles as dry cleaning soaps are the *rug cleaning soaps*:

H.	Oleic acid	28 lbs.
	Ethylene dichloride	13
	Isopropanol, 99%	14
	Butyl Cellosolve	5
	Triethanolamine	16
	Water	125

1. Mix the oleic acid, ethylene dichloride, isopropanol, and butyl Cellosolve, and add the amine.

2. Stir until thoroughly mixed and add the water. If the mixture is cloudy, add sufficient isopropanol to clear it.

3. Use an emulsion made of equal volumes of the soap and water for cleaning rugs and carpets.

Adequate ventilation should be provided, and special care should be taken to avoid inhaling vapor and repeated contact with the skin whenever chlorinated solvents are used.

What are the demands made on a good dry cleaning soap? They are especially exacting for a soap used when the solvent in the dry cleaning process is subsequently recovered by filtration. Not only must the soap be easily soluble in the solvent without separation, but also it should not form a gelatinous deposit that would obstruct the filter after a short period and prevent any further recovery of the solvent. When using the distillation method of recovery this factor is not so important, but in any case these demands should be kept in mind.

The effectiveness of the dry cleaning soap as a soap should be exceptional, *i.e.*, dirt should be dissolved or dispersed and the material prepared for penetration of the solvent; also, water should be well bound. An important factor is whether the laundry concerned uses petroleum solvents or chlorinated hydrocarbons in the dry cleaning process. When they are used as the main solvent or as an addition, such solvents should also be used in the manufacture of the dry cleaning soaps. It would not be correct at this point to pass on to a new subject without mentioning the importance of synthetic detergent materials available for use as dry cleaning and solvent soaps, *e.g.*, the triethanolamine salt of a sulfated lauryl alcohol. These materials[6] are becoming very important in this field because of their good solvent and detergent properties.[4a] To this class we must add the pure emulsifiers used with or without additional detergent aid to bind moisture and make solvent-to-textile contact more thorough. Some of these emulsifiers, such as the polyethylene oxide condensates of fatty acids, are designed for use on specified solvent cleaners.

Fabry[7] has enumerated the following prime requisites for a dry cleaning soap: (*1*) stability in composition; (*2*) no objectionable odors in the soap itself, nor should the soap contribute any odors to the garments; (*3*) the soap should cause a minimum amount of pressure in the filter and not corrode the equipment; (*4*) it should increase the electrical conductivity of the solvent, or be an antistatic agent; (*5*) it should possess a high degree of both inert insoluble soil and water-soluble soil removal power; (*6*) it should not discolor the solvent; (*7*) it should produce a minimum amount of foam. Foam is not desirable in the dry cleaning process, particularly where solvent is recovered by distillation means.

[6] And many other types of synthetic detergents.

[7] A. Fabry, *Soap*, 22, No. 7, 49 (1946).

U.S. National Bureau of Standards specification for a "Stoddard solvent," widely used in dry cleaning, is as follows: (a) appearance shall be clear and free from susupended matter and undissolved water; (b) color shall be water white or not darker than 2i by the Saybolt chromatometer; (c) odor shall be sweet; (d) flash point not lower than 100°F.; (e) corrosion test: a clean copper strip shall show not more than an extremely slight discoloration, when submerged in solvent for three hours at 212°F.; (f) distillation range: not less than 50% at 350°F.; the dry or end point not above 410°F.; no tolerance shall be allowed above 410°F.; (g) acidity: the residue after distillation shall not show acid reaction; (h) doctor test shall be negative. (i) sulfuric acid absorption test: not more than 5% of solvent absorbed by sulfuric acid (sp. gr. 1.835).

Other solvents used both as prime solvents in dry cleaning and as solvents for the manufacture of solvent soaps and dry cleaning soaps, are listed in Table XX-1,[8] with their more important characteristics.

(C) THE TOXICITY OF SOLVENTS

The classification of solvents on the basis of their toxicity, according to Brandt *et al.*,[9] is as follows:

1. *Aromatics.* These materials are very toxic. The common ones have the maximum allowable concentration of 50 to 200 p.p.m. in air. Examples are benzene, toluene, and xylene.

2. *Halogenated Hydrocarbons.* These also are very toxic. Most of those encountered in the group of solvents used for dry cleaning, etc., fall into a maximum allowable concentration in the range of 50 to 200 p.p.m. Examples are carbon tetrachloride, trichloroethylene, and dichlorobenzene.

3. *Alcohols, Esters, Ethers, and Ketones.* These chemical groups are less toxic than groups 1 and 2. Most of those encountered fall into a maximum allowable concentration toxicity range of 200 to 400 p.p.m. Examples are acetone, methyl ethyl ketone, the alcohols, and the acetates.

4. *Paraffins and Naphthenes.* This group is not particularly toxic. It includes materials such as gasoline, Stoddard solvent, petroleum naphtha, etc. The maximum allowable concentration for these range from 500 to 1000 p.p.m.

With regard to the effect of solvents on the skin, we want to point out that, in principle, the aromatic solvents and the chlorinated hydrocarbons are more irritating than the solvents of groups 3 and 4, but generally, solvents may cause dermatitis very easily. In any case, small dosages of solvent

[8] The table is a modified and adapted version of tables published in *Ind. Eng. Chem.*, 27. 1169–1179 (1935).

[9] A. D. Brandt, W. J. McConnell, and R. H. Flinn, *U. S. Public Health Reports*, 61, 132–143 (1946).

TABLE XX-1

No.	Compound	Formula	Mol. wt.	Boiling range		Flash pt., °F	Vapor press., 30°C., mm. Hg
				Init. b. p., °C.	End pt., °C.		
		HYDROCARBONS					
1	Benzene	C_6H_6	78.05	78	81	< 5.5	118
2	Toluene	$C_6H_5CH_3$	92.06	109	111	44	26
3	Xylene	$C_6H_4(CH_3)_2$	106.08	127	159	80	11
4	Hi-Flash naphtha	....	—	149	193	115	—
5	V. M. & P. naphtha	....	—	105	155	< 60	—
6	Mineral spirits	....	—	152	207	> 100	—
7	Cyclohexane	C_6H_{12}	84.09	80	83	< 6.5	121
8	Tetrahydronaphthalene (Tetralin)	$C_{10}H_{12}$	132.09	196	217	180	< 1
9	Decahydronaphthalene (Decalin)	$C_{10}H_{18}$	138.14	186	194	145	2
		NAVAL STORES SOLVENTS					
10	Gum spirits of turpentine	....	—	154	201	110	—
11	Steam distilled turpentine		—	155	173	115	—
12	Dipentene	$CH_2(C_3H_5)C:(CH_3)CH_3$	136.13	172	200	145	2
13	Hercosol		—	176	262	150	—
14	Pine oil		—	99	226	185	—
15	Heavy pine oil		—	211	219	200	—
16	Fenchone	$(CH_3)_2C_6H_7C:O$	152.13	190	210	160	2
		CHLORINATED COMPOUNDS					
17	Ethylene dichloride	$ClCH_2CH_2Cl$	98.95	82	84	70	94
18	Monochlorobenzene	C_6H_5Cl	112.50	130	134	95	15
19	Orthodichlorobenzene	$C_6H_4Cl_2$	146.95	177	180	175	3
20	Dichloroethyl ether	$ClCH_2CH_2OCH_2CH_2Cl$	142.98	172	178	178	2
21	Trichloroethylene	$CHCl:CCl_2$	131.4	85	87	Nonflam.	56 at 20°
22	Carbon tetrachloride	CCl_4	78	77	77	Nonflam.	90.6 at 20°
		ALCOHOLS					
23	Methanol (anhydrous)	CH_3OH	32.03	64	66	52	160
24	Ethanol (anhydrous)	C_2H_5OH	46.05	77	79	65	78
25	Isopropanol (anhydrous)	$(CH_3)_2CHOH$	60.06	82	83	67	60
26	sec-Butanol	$CH_3CH_2CHOHCH_3$	74.08	96	103	88	26
27	Isobutanol	$(CH_3)_2CH_2CHOH$	74.08	107	111	111	17
28	n-Butanol	C_4H_9OH	74.08	116	119	111	11
29	sec-Amyl alcohol	$(CH_3CH_2)_2CHOH$	88.09	117	124	110	12
30	Amyl alcohol (mixed isomers)	$C_5H_{11}OH$	88.09	121	139	111	—
31	Methyl amyl alcohol	$(CH_3)_2CHCH_2CH(CH_3)OH$ ..	102.11	131	132	114	6
32	Hexyl (2-ethylbutyl) alcohol	$CH_3CH_2CH(C_2H_5)CH_2OH$	102.11	144	156	145	4
33	Octyl (2-ethylhexyl) alcohol	$C_4H_9CH(C_2H_5)CH_2OH$	130.14	182	201	178	< 1
34	Cyclohexanol	$C_6H_{11}OH$	100.09	150	182	170	2
35	Methylcyclohexanol	$CH_3C_6H_{10}OH$	114.18	170	180	159.4	1 (20°)
		ETHER ALCOHOLS					
36	Methyl Cellosolve	$CH_3OCH_2CH_2OH$	76.06	121	126	105	< 2
37	Cellosolve*	$C_2H_5OCH_2CH_2OH$	90.08	133	137	111	7
38	Isopropyl Cellosolve	$(CH_3)_2CHOCH_2CH_2OH$	104.09	140	143	125	8
39	Butyl Cellosolve	$C_4H_9OCH_2CH_2OH$	118.11	163	172	165	2
40	Methyl Carbitol	$CH_3OCH_2CH_2OCH_2CH_2OH$	120.09	190	194	200	< 1
41	Carbitol*	$C_2H_5OCH_2CH_2OCH_2CH_2OH$ ..	134.11	189	203	205	< 1
42	Butyl Carbitol	$C_4H_9OCH_2CH_2OCH_2CH_2OH$ ..	162.14	220	231	230	< 1
43	Benzyl Cellosolve	$C_6H_5CH_2OCH_2CH_2OH$	152.09	254	258	265	< 1
		ESTERS					
44	Ethyl acetate	$CH_3COOC_2H_5$	88.06	70	80	35	121
45	n-propyl acetate	$CH_3COOCH(CH_3)_2$	102.08	84	94	35	74
46	Isopropyl acetate	$CH_3COOCH(CH_3)_2$	102.08	82	90	45	—
47	Ethyl propionate	$CH_3CH_2COOC_2H_5$	102.08	90	118	70	43
48	sec-Butyl acetate	$CH_3COOCH(CH_3)(C_2H_5)$	116.09	105	127	88	29
49	Isobutyl acetate	$CH_3COOCH_2CH(CH_3)_2$	116.09	114	118	88	27
50	n-Butyl acetate	$CH_3COOC_4H_9$	116.09	119	127	88	16
51	sec-Amyl acetate	$CH_3COOCH(CH_3)(C_3H_7)$	130.11	121	144	111	10
52	Amyl acetate (mixed isomers)	$CH_3COOC_5H_{11}$	130.11	127	155	111	9
53	Cellosolve acetate	$C_2H_5OCH_2CH_2OOCCH_3$	132.09	145	166	122	3
54	Butyl Cellosolve acetate	$C_4H_9OCH_2CH_2OOCCH_3$	160.12	188	192	180	< 1
55	Methyl Carbitol acetate	$CH_3OCH_2CH_2OCH_2CH_2OOCCH_3$	162.11	203	212	180	< 1
56	Carbitol acetate	$C_2H_5OCH_2CH_2OCH_2CH_2OOCCH_3$	176.12	211	220	225	< 1
57	Butyl Carbitol acetate	$C_4H_9OCH_2CH_2OCH_2CH_2OOCCH_3$	204.16	236	249	260	< 1
		POLYETHERS					
58	Diethyl Cellosolve	$C_2H_5OCH_2CH_2OC_2H_5$	118.11	119	125	90	22
59	Diethyl Carbitol	$C_2H_5OCH_2CH_2OCH_2CH_2OC_2H_5$	162.14	181	189	170	1

* Trade name.

TABLE XX-1 (*continued*)

No.	Sp. gr., 20°C.	Wt./gal., 20°C., lb.	Refr. index, 20°C.	Coeff. of expan., 10–30°C.	Purity com. prod., %	Dilution ratio				Solubility by wt., 20°C.	
						Toluene	Petrol. naphtha	Xylene	Min. spir.	In water	Water in
HYDROCARBONS											
1	0.878	7.31	1.5014	0.00124	—	—	—	—	—	0.19	Insol.
2	0.866	7.21	1.4962	0.00107	—	—	—	—	—	0.05	Insol.
3	0.862	7.17	—	0.00099	—	—	—	—	—	v.s.s.	Insol.
4	0.860	7.16	—	0.00094	—	—	—	—	—	v.s.s.	Insol.
5	0.763	6.36	—	0.00098	—	—	—	—	—	v.s.s.	Insol.
6	0.769	6.40	—	0.00098	—	—	—	—	—	v.s.s.	Insol.
7	0.779	6.48	1.4273	0.00108	—	—	—	—	—	v.s.s.	Insol.
8	0.972	8.09	1.5461	0.00083	—	—	—	—	—	v.s.s	Insol.
9	0.885	7.37	—	0.00088	—	—	—	—	—	v.s.s.	Insol.
NAVAL STORES SOLVENTS											
10	0.868	7.22	—	0.00090	—	—	—	—	—	v.s.s.	Insol.
11	0.857	7.13	—	0.00089	—	—	—	—	—	v.s.s.	Insol.
12	0.853	7.10	1.473	0.00086	—	—	—	—	—	v.s.s.	Insol.
13	0.912	7.59	—	0.00083	—	0.4	0.1	—	—	v.s.s.	Insol.
14	0.925–0.935	7.7	—	0.00066	—	—	—	—	—	v.s.s.	1.7
15	0.937–0.942	7.8	—	0.00085	—	—	—	—	—	v.s.s.	2.4
16	0.948	7.89	1.4647	0.00088	—	—	—	2.9	0.8	0.2	0.5
CHLORINATED COMPOUNDS											
17	1.256	10.45	1.444	0.00116	99	—	—	—	—	0.87	0.16
18	1.108	9.22	1.525	0.00092	99	—	—	—	—	v.s.s.	Insol.
19	1.308	10.88	1.549	0.00083	99	—	—	—	—	v.s.s.	Insol.
20	1.222	10.17	1.457	0.00097	99	—	—	—	—	1.02	0.1
21	1.470	12.25	1.481	—	—				—	0.1	—
22	1.594	13.28	1.463	0.001236	—				—	0.08	—
ALCOHOLS											
23	0.793	6.60	1.329	0.00118	99	2.5	0.3	—	—	∞	∞
24	0.791	6.58	1.361	0.00108	99	—	—	—	—	∞	∞
25	0.786	6.54	1.3776	0.00107	99	—	—	—	—	∞	∞
26	0.808	6.72	1.397	0.00091	99	—	—	—	—	12.5	44.1
27	0.803	6.68	1.396	0.00095	99	—	—	—	—	10	16.9
28	0.811	6.75	1.3974	0.00094	99	—	—	—	—	8.0	19.5
29	0.810	6.74	—	0.00088	95	—	—	—	—	0.13	9.87
30	0.814	6.77	—	0.00093	99	—	—	—	—	0.09	8.98
31	0.807	6.72	1.4087	0.00100	99	—	—	—	—	1.73	6.37
32	0.833	6.93	1.4229	0.00089	99	—	—	—	—	0.63	4.56
33	0.834	6.94	1.4300	0.00088	99	—	—	—	—	0.06	2.48
34	0.951	7.92	1.4656	0.00077	94	—	—	—	—	0.13	11.78
35	0.922	7.75	1.4635	—	—	—	—	—	—	v.s.s.	—
ETHER ALCOHOLS											
36	0.966	8.04	1.4028	0.00094	99	4.0	Imm.	2.9	Imm.	∞	∞
37	0.931	7.75	1.4080	0.00097	99	4.9	1.1	4.3	0.7	∞	∞
38	0.906	7.53	—	0.00093	97	4.3	1.6	3.8	1.3	∞	∞
39	0.902	7.50	1.4190	0.00087	99	3.5	2.3	3.2	1.9	∞	∞
40	1.035	8.62	1.4244	0.00087	—	—	—	1.0	Imm.	∞	∞
41	1.027	8.55	—	0.00082	—	—	—	1.2	Imm.	∞	∞
42	0.955	7.95	1.4290	0.00087	96	—	—	4.2	1.2	∞	∞
43	1.070	8.90	—	0.00076	99	—	—	3.0	Imm.	0.4	18.1
ESTERS											
44	0.886	7.37	1.3727	0.00134	85	3.3	1.1	—	—	6.92	11.01
45	0.870	7.23	1.3770	0.00132	95	2.7	1.1	—	—	2.58	2.86
46	0.857	7.13	—	0.00119	85	3.0	1.2	—	—	2.78	5.58
47	0.891	7.41	1.3844	0.00125	96	2.1	0.8	—	—	1.92	1.22
48	0.858	7.14	1.389	0.00118	82	2.2	1.2	—	—	0.62	1.65
49	0.870	7.24	1.3997	0.00119	96	2.7	1.1	—	—	0.67	1.64
50	0.876	7.29	1.3951	0.00117	90	2.9	1.3	2.7	1.3	0.43	1.86
51	0.862	7.18	—	0.00114	92	2.2	1.0	2.0	0.6	0.19	0.88
52	0.862	7.17	—	0.00104	84	2.1	1.2	—	—	0.17	1.15
53	0.974	8.10	1.4030	0.00111	96	2.5	0.9	2.3	0.7	24.7	9.4
54	0.943	7.85	—	0.00104	99	—	—	1.9	1.0	0.9	1.9
55	1.040	8.65	—	0.00099	99	—	—	1.7	0.3	∞	∞
56	1.011	8.41	1.4230	0.00101	97	—	—	1.9	0.6	∞	∞
57	0.987	8.21	—	0.00094	99	—	—	1.8	0.6	1.6	3.4
POLYETHERS											
58	0.849	7.07	—	0.00120	95	—	—	0.4	0.2	2.76	4.48
59	0.909	7.56	—	0.00106	99	—	—	1.4	0.5	∞	∞

fumes taken repeatedly over a long period of time can lead to serious poisoning effects and should be avoided at all costs. The effects can be cumulative. Absorption by the skin is dangerous as well, aside from the effect of dermatitis.

(2) Textile Soaps

Soaps and soaplike assistants for the textile industries represent an enormous field in themselves, for each special soap for the different textiles and stages in textile processing has an individual character. It is beyond the scope of this book to deal with modern "nonsoap" detergents and textile assistants that are used in the textile industry today. Still, soap is one of the most important detergents for the textile industry, and it is estimated that in America today, even with the synthetics thoroughly entrenched in the textile field, soap still commands over 50% of the business by volume of pounds consumed.

Many different soaps and soap preparations represent a field wide enough to warrant careful consideration by any progressive soapmaker who wants to widen his market.

Ordinary textile soaps without the addition of solvents, are prepared in the usual manner by saponification of fats or fatty acids with alkalies. In the case of wool, special soaps are used for washing the raw wool to remove the crude wool fat. Soda soaps as well as the potash soaps are effective for this purpose (the latter chiefly for finer counts of wool). The detergent power of the soaps is frequently improved by addition of soda, ammonia, or other alkaline soap builders. But it would be better to deliver soap to the user free of all such ingredients, which could be subsequently added as required in the appropriate amounts.

As a matter of fact, soap has the handicap of forming lime and magnesia soaps in *hard* water, and it is thus of great importance to use *soft* water in all textile processes employing soap. Also, soap hydrolyzes in water, forming free alkalinity and fatty acids and/or acid soaps. This hydrolysis of soap has its effect on the textile fiber, and it is the textile fiber itself which determines to a great extent the action of the soap.[10]

When soap splits up in water into alkali and fatty acid, the wool absorbs more alkali than acid and so becomes alkaline even from a neutral soap. Removal of the alkali leaves free fatty acid, so that the bath becomes charged with acid soap which is deposited on the wool; this effect is greater in dilute solutions as there is less soap available for the removal of the fatty deposit. This absorption of alkali from soap solutions is such that wool may "kill" a soap solution, and for this reason it is customary to employ small amounts of alkali with soap for certain purposes.

[10] J. T. Marsh, *An Introduction to Textile Bleaching*, Chapman & Hall, London, 1946, p. 132.

This quotation from Marsh shows clearly the problem of using soaps in the textile industry with regard to alkalinity. But it is exaggerated when he states that "excessive amounts of alkali, however, will precipitate soap." Such a surplus is practically never reached in textile scouring and even textile "kiering."

Of some of the main textile treatments where soaps find application,[11] the *scouring process of cotton* should be mentioned. Cotton is a fiber that is very resistant to alkalies and the soaps used for the scouring process are used in strong alkaline wash liquors. These soaps are very often alkaline themselves, *i.e.*, they may have a high percentage of free alkali. The alkalinity of the scouring liquors in the kiering process may be from 2–3 Tw. NaOH (0.9– 1.35%) for lightweight fabrics. Temperatures may be as high as 100–125°C. and pressure may be used as well. The soaps used in these processes are either rosin soap or soap of the Marseille type. Very often, solvent soaps containing cyclohexanol, hexalin, methylcyclohexanol, methylhexalin, tetrahydronaphthalene (tetralin), and decahydronaphthalene (decalin) as well as pine oil are used—these have been described in Section 1, A, on solvent soaps. These solvent soaps have a certain dispersing power for lime soaps as well, so that they are especially suited for kiering in hard water.

Scouring of wool to free it from fat and wax is a process which must be carried out under mild conditions. Alkalinity must be low, and temperatures are usually between 40 and 50°C. The principles for the choice of a suitable soap are clearly described by Marsh.[12]

The *exact* neutrality of a soap for scouring, as distinct from milling, is sometimes over-stressed in considering raw wool; small quantities of alkali have beneficial effects on the scour, but it is important that no free alkali should be left in the wool at the conclusion of the scour. The very dilute nature of the scouring liquor also provides a safeguard in itself.

It is frequently assumed that the best soap for scouring is a potash–olive oil soap but some cheaper alternatives are available. The hardness or softness of a soap is not solely decided by its alkali constituent: the fatty acid also plays its role. Palmitic and stearic acids are solids at ordinary temperatures and their soaps are not very soluble in cold water and tend to gelatinize. Oleic acid, on the other hand, is liquid at room temperatures and yields soaps which are very soluble and do not gelatinize. The harder soaps are more difficult to remove from the wool and their residues tend to give a harsh feel to the scoured material. A satisfactory substitute for the potash–olive oil soap is a soda soap made from olein which is free from the solid fatty acids and sufficiently free from stearine in particular to have a low melting-point; this may be tested in a simple manner by observing the tendency to gelatinize on cooling the soap solution or, alternatively, by precipitating the fatty acid from the soap and observing the melting-point which should not exceed 27 to 30°C.

Part of the detergent action of soap is due to the reduction of the interfacial tension

[11] J. Davidsohn and A. Davidsohn, *Soap, Perfumery, and Cosmetics, 12,* 417–420 (1939).

[12] J. T. Marsh, *loc. cit.,* p. 305.

between the scouring liquor and the wool grease; the surface tension effect increases rapidly with concentration up to 0.4% after which there is little further improvement. A second factor is the stabilizing effect due to its action as a protective colloid, and this is at a maximum around 0.2 to 0.3%. It would appear, therefore, that there is no advantage in exceeding a concentration of 0.4% soap; actually 0.7% soap is frequently used in the first bowl.

As soap hydrolyzes in aqueous solution,[13] the wool fiber tends to absorb alkali preferentially from the washing liquor, besides, wool grease is slightly acid itself and the washing liquor will tend to become acid. This is very often corrected during the scouring process itself, *e.g.*, by adding about 0.25% sodium carbonate to the wash liquor. As already pointed out wool is susceptible to alkali and the conditions of alkalinity must be carefully controlled. But the danger is very small:

With the very dilute solutions employed in wool scouring there is less risk of damage; sodium carbonate in solution up to 5% concentration gave no appreciable tendering in one hour at 50°C. Strong solutions of soap have tendering actions equal to that of about one-fifth of the equivalent of caustic soda, and appreciable tendering is produced in an hour at 50°C. by either 1.5% sodium oleate or 0.04% sodium hydroxide. An average concentration of 0.5% soap, as commonly employed, is well below these figures, and even a soap containing 4% of alkali will not produce tendering provided it is neutralized before the wool is dried. Sodium carbonate, of course, is safer than the hydroxide which is completely ionized in aqueous solution at room temperatures.

Usually, wool scouring soaps may be soft soaps of the transparent fig or silver type. A description is unnecessary here, since these soaps are already described in detail in Chapter XIX. But low titer hard soap (*e.g.*, flakes) is often used as well. The use of sodium tetraphosphate, $Na_6P_4O_{13}$, in a percentage of about 10% calculated on the soap used has given excellent results. The amount of soap saved by preventing lime soap precipitation was about 25%.[14] The scouring effect is especially good and the strength of the wool fiber is less impaired.

The process in which soap is used extensively is the so-called *milling* or *felting process* for wool, which brings about the felting of the wool fabric. The main process employed is the *alkaline milling* process. (In the acid milling process no soap can be used.) At a pH of about 10, felting of wool is the most rapid and with soap and alkaline soap builders the process may be carried out most effectively at temperatures of about 35–40°C. Soap milling is probably the most common type of milling and takes place on fabrics which have already been scoured to some extent; 5 to 10% of soap is required, depending on the extent of milling.

The titer of the fatstock used is of great importance for milling soaps. A high titer soap encourages felting and the soap does not "run" during the

[13] J. T. Marsh, *loc. cit.*, pp. 305–307.
[14] A. H. Razee, *Textile World*, **95**, No. 9, 155–157, 230–234; No. 10, 120–123, 215-224 (1945).

TABLE XX-2

Constituent	Good	Medium	Cheap
Tallow	47	31	25
Palm oil	11	10	8
Na_2CO_3 (66 Tw.)	6	9	11
NaOH (66 Tw.)	31	26	25
Silicate	—	9	17
Starch	—	—	1
Water	5	15	13
Total	*100*	*100*	*100*

milling process. But as temperatures are usually moderate this "hardness" of the soap is very often overestimated. A compromise must be found between good solubility even in colder water, good rinsability, and harder structure of the fatstock. Often synthetic detergents are used in conjunction with soap.

Some compositions of milling or felting soaps are given in Table XX-2.[15] As the amount of sodium silicate increases, the ease of rinsability decreases. Other examples, according to older German specifications, are given in Table XX-3.

TABLE XX-3

NEUTRAL FULLING SOAPS

Hard Soaps

Total fatty acids	Min.	60.0%
Free alkali, calc. as NaOH	Max.	0.1
Unsaponifiable and unsaponified fat	Max.	1.5
Alkali carbonate, calc. as Na_2CO_3	Max.	0.5
Insol. in alcohol	Max.	2.0

Soft Soaps

Total fatty acid hydrate content	Min.	40.0
Free alkali, calc. as KOH	Max.	0.15
Unsaponifiable and saponifiable fat	Max.	1.5
Alkali carbonate calc. as K_2CO_3	Max.	2.0
Insol. in alcohol	Max.	4.0

ALKALINE FULLING SOAPS

Hard Soaps

Total fatty acid hydrate content	Min.	60.0%
Free alkali, calc. as NaOH	Max.	1.5
Unsaponifiable and unsaponified fat	Max.	1.5
Alkali carbonate calc. as Na_2CO_3	Max.	3.0

Soft Soaps

Total fatty acid hydrate content	Min.	40.0
Free alkali calc. as KOH	Max.	1.5
Unsaponifiable and unsaponified fat	Max.	1.5
Alkali carbonate, calc. as K_2CO_2	Max.	5.0

[15] *Dyer*, *90*, 210 (1943).

Typical formulas are given by Grant:[16]

A good grade of soap is made with the following ingredients:

Grease or tallow	535 lbs.
Palm oil	125 lbs.

Heat these to 118°F. Then add:

Caustic soda lye (36° Bé)	360 lbs.
Soda ash solution (33° Bé or over)	75 lbs.
Water	50 lbs.

The following ingredients will make a slightly cheaper grade of fulling soap:

Grease or tallow	400 lbs.
Palm oil	200 lbs.

Heat these to 110°F. Then add:

Caustic soda lye (36° Bé)	335 lbs.
Soda ash solution (33° Bé or over)	50 lbs.
Water	170 lbs.

A fair grade of fulling soap will result if the following ingredients are used:

Grease or tallow	375 lbs.
Palm oil	125 lbs.

Heat to 110°F. Then add:

Caustic lye (36° Bé)	315 lbs.
Silicate of soda	100 lbs.
Soda ash solution (33° Bé or over)	100 lbs.
Water	170 lbs.

The ingredients stated below will give a cheap fulling soap:

Tallow or grease	300 lbs.
Palm oil	100 lbs.

Warm until liquid, but keep it cool. Then add:

Caustic soda lye (36° Bé)	300 lbs.
Silicate of soda	200 lbs.
Soda ash solution (33° Bé or over)	130 lbs.
Water	160 lbs.
Starch	10 lbs.

These soaps are prepared by the semiwarm process. It must be pointed out that they may be prepared from the same fatstock as fully boiled and grained-out soaps. A special variety of fulling soap is the solid potash soap containing up to 50% total fatty acids. This is generally an alkaline product (0.5% KOH as a rule).

Fats used in these soaps are divided into those giving high viscosity, and those giving low viscosity solutions. Examples of the former are: 83% bone fat, 17% coconut oil fatty acids, or 68% bone fat, 17% palm oil, and 15%

16 F. L. Grant, *Soap, Perfumery & Cosmetics Year Book,* London, 1936, pp. 114–116.

palm kernel oil. Fat mixtures of the second class may comprise 50% bone fat, 23% palm oil, 12% lard, and 15% lower grade coconut oil; or 40% bone fat, 30% palm oil, 13% lard, and 17% palm kernel oil. Strong lye is used in preparing the soap, because a high percentage product is intended. (The soap yield amounts to roughly 200% calculated on the raw fats, as compared with 250% for an ordinary soft soap.) A proportion of approximately 30 kg. of potassium carbonate is allowed for each 100 kg. of 50° Bé KOH.

These soaps are usually prepared by the semiboiled process. Their consistency may be improved by additions of potassium salts. Unfortunately, the cheap inorganic potassium salts such as potassium chloride and potassium carbonate are less suitable than more expensive organic potassium salts (lactates, acetates, and formates). But an addition of only 1% potassium formate has a very good effect on the soap, so the price of this salt is not so very important. The solid potassium soaps are usually transparent; they have an excellent foam and detergent quality; they are easily soluble; but they are somewhat hygroscopic and are best packaged to prevent absorption of water from the air.

In many ways the solid potassium soaps represent the compromise mentioned above between solubility in moderately warm or even cold water, rinsability, and hard structure of the fatstock.

It must be mentioned that, especially in texile processes, where some soap may remain in the fiber, the fatstock should be composed of light-colored fats and oils; otherwise, discoloration of the cloth may occur. Besides, fatstocks for such textile soaps should not give soaps liable to rancidity, as it was found that rancidity not only gives rise to discoloration and bad odor but actually harms the fiber.

Another textile process in which soap is important is the *degumming process for silk:*[17]

The common method of removing the gum from raw silk is to treat the fibers in a moderately concentrated solution of soap. The degumming operation is sometimes termed "boiling-off," but in actual fact, the silk is not boiled, and the temperature is, in general, maintained at about 95°C., for the act of ebullition is apt to disturb the fine filaments and bring about entanglements and damage; some chemical damage may also result from the higher temperature.

If the whole of the gum has to be removed, it is necessary to prolong the process, and also to use fresh solutions of soap. The concentration of the soap in the bath and also the number of baths are determined by the amount of sericin, which has to be removed.

The amount of silk gum, or sericin, varies between 20 and 30% and it is either partly or completely removed from raw silk, with a corresponding loss in weight. For this purpose, pure olive oil soda soaps (Marseilles soaps) with a 62 to 65% total fatty acid content are the best. Possible substi-

[17] J. T. Marsh, *loc. cit.,* p. 379.

tutes for olive oil are sesame, cottonseed, and groundnut oils. Soft soaps derived from olive, groundnut, sesame, or red oil are also commonly used in the handling of raw silk. Incidentally, a first class olive oil is not always indispensable, but may be replaced by olive oil foots. Coconut oil is sometimes used in the fatstock of soap for silk washing. High titer fats are less suitable. The amount of soap employed is usually calculated on the weight of material and is as high as 20–50%.

Very frequently, the mills recover their soaps by passing the waste liquor to acidulating tanks, skimming off the fatty acids, and reconverting them to soaps.

Alkaline soap builders are often used in conjunction with soap. Addition of a synthetic detergent, Nacconol NR,[18] or another sodium alkyl aryl sulfonate (about 20%, calculated on the neutral soap used) gives especially good results in combination with alkaline soap builders. Soap in conjunction with synthetic detergents is well suited for scouring alkali-sensitive *rayon*. But rayon may also be treated with a 0.3–0.5% solution of soap (similar in type as for silk), to which some sodium carbonate and/or trisodium phosphate may be added as well. It is possible to produce a ready-made soap for this purpose containing some 3–5% trisodium phosphate. Combinations of soaps with non-ionic detergents have recently found entrance into the textile industry.

(3) Abrasive and Scrubbing Soaps

There are two main types of such soaps on the market: (1) scrubbing soaps such as hand cleaners and (2) soap powders or pastes for cleaning of pots, pans, tiles, floors, windows, etc. The latter types are used more widely and these products are dealt with first.

The following (U. S.) Federal Specification[19] is an example of the composition and use of such compounds:

Cleaning compound (*PC-565*) *soap*—abrasive type for painted surfaces.

The product is to be without objectionable odor, and not harmful to the hands. The seller must label each container with directions for use. The product must be capable of being applied either with a damp cloth or sponge. It is to be a uniform soft paste, meeting the following requirements.

Matter volatile at 105°C. shall not exceed 65% by weight. It shall contain not more than 0.1% by weight of free alkali calculated as NaOH. It shall contain not more than 0.5% by weight free acid calculated as oleic acid. Alkaline salts calculated as Na_2CO_3 shall not exceed 5% by weight. Insoluble siliceous matter shall not be less than 25% nor more than 50% by weight. All of the insoluble siliceous matter shall pass through a No. 80 sieve; and not more than 15% shall be retained on a No. 200 sieve. Anhydrous

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[18] National Aniline Div., Allied Chemical & Dye Corp.

[19] Federal Specification PC-565 Cleaning Compound, U. S. Government Printing Office, Washington 25, D. C.

soap shall be not less than 3.5% by weight. Total glycerol content shall not exceed 0.8% of the weight of anhydrous soap contained in this product.

A special test is provided for determination of abrasive properties. A thin film of the compound is spread over a clear microscopic slide. Another slide is placed over the film and the two slides pressed together, using a slight pressure, and rubbing one slide over the other with a rotary motion. The slides when wiped clean of the compound shall not be scratched.

This product may be manufactured on the basis of a mixture of soft soap, soda ash, waterglass, and abrasive as follows: 200 parts transparent soft soap, 30 parts of pumice, 3 parts soda ash, 2 parts waterglass of 38° Bé (Na_2O : *ca.* $3SiO_2$) dissolved in 25 parts water, 20 parts of a *ca.* 5% aqueous starch solution.

The abrasive and alkaline builders are incorporated into the soft soap in a kneading or similar mixing machine. The starch solution previously prepared is then added to the mixture in the machine. Within the limits of the specification, many combinations are possible; the formula cited is meant only as an example.

A scouring powder usually consists of a uniform mixture of soap powder and an insoluble abrasive. The abrasive is usually powdered pumice, volcanic ash, quartz, marble, or feldspar. The abrasive is mixed with the soap and sodium carbonate in a special mixer.

Some further U. S. Federal Specifications illustrate the composition and use of such products:

Scouring powder for floors (PP-591).
Scouring powder for floors shall be of the following types, as specified: Type A—for fine marble floors; Type B—for tile or ceramic and terrazzo floors; Type C—soap scouring compound.
Type A (for fine marble floors) :
Matter volatile at 105 to 110°C. shall not exceed 10%. Deliveries which yield more than 10% of volatile matter shall be rejected without further test. The sum of sodium carbonate (Na_2CO_3) and anhydrous soap shall not exceed 7% nor be less than 2 per cent. Free alkali, calculated as sodium hydroxide (NaOH) shall not exceed 0.1%. Insoluble siliceous material shall be not less than 85% nor more than 95%. All of the insoluble siliceous material shall pass through a No. 100 sieve, and the residue retained on a No. 200 sieve shall not exceed 5%. The material shall not scratch nor discolor marble. The material shall be a uniform powder, shall be unscented, and shall be of a light grey or white color. Total glycerol content shall not exceed 0.8% of the weight of anhydrous soap contained in this product.
Type B (for tile or ceramic and terrazzo floors) :
Matter volatile at 105 to 110°C. shall not exceed 10%. Deliveries which yield more than 10% of volatile matter shall be rejected without further test. The sum of sodium carbonate (Na_2CO_3) and anhydrous soap shall not be less than 2%. Free alkali, calculated as sodium hydroxide (NaOH), shall not exceed 0.1%. Insoluble siliceous material shall be not less than 80 nor more than 95%. The insoluble siliceous material shall not yield more than 1% of residue retained on a No. 60 sieve and not more than 10% of residue retained on a No. 80 sieve. The material shall be a uniform powder, shall be

unscented, and shall be of a light grey or white color. Total glycerol content shall not exceed 0.8% of the weight of anhydrous soap contained in this product.

Type C (soap scouring compound):

Matter volatile at 105 to 110°C. shall not exceed 6%. Deliveries which yield more than 6% of volatile matter shall be rejected without further test. Carbonated alkali, calculated as sodium carbonate (Na_2CO_3) shall not be less than 6% nor more than 20%. Free alkali, calculated as sodium hydroxide (NaOH), shall not exceed 0.1%. Anhydrous soap shall be not less than 3% nor more than 10%. Insoluble siliceous material shall be not less than 60% nor more than 90%. The insoluble siliceous material shall not yield more than 1% of residue retained on a No. 60 sieve and not more than 10% of residue retained on a No. 80 sieve. The material shall be a uniform powder, shall be unscented, and shall be light grey or white in color. Total glycerol content shall not exceed 0.8% of the weight of anhydrous soap contained in this product.

Some formulas which may serve as basis for the manufacture of the specified scouring powders follow:

Scouring powders for floors (PP-591).
Type A:
        4 parts sodium carbonate
        3 parts powdered curd soap
        93 parts of abrasive powder as specified in the sieve test consisting of pumice, feldspar, etc.
Type B:
        5 parts sodium carbonate
        8 parts powdered curd soap
      87 parts of abrasive powder with properties as specified

In types *A* and *B* it is possible to incorporate 7–8% water (calculated on the whole mixture). Incorporation of water must be by a very fine spray so as to avoid caking. The prepared mixture should pass through a fine pulverizing mill. If a good powder mill is used, coarser grades of abrasive may be used that will be ground in the mill to the required fineness. Careful control of fineness and drying loss is indispensable.

Type C:
        12 parts sodium carbonate
        7 parts powdered curd soap
        91 parts abrasive
     Scouring powder for glass (PP-596a):
        4 parts sodium carbonate
        6 parts powdered curd soap (without rosin)
        90 parts abrasive with properties as specified

In a comprehensive article on abrasive cleansers, Lesser[20] gives some formulas for kitchen purposes. Typical of such compositions is the following product, described[21] as useful for cleaning kitchen utensils, sinks, and other

20 M. A. Lesser, *Soap, 21*, No. 6, 44–47 (1945).
21 D. F. Mason, *Chem. Ind., 45*, 50 (1939).

objects not injured by strong abrasives and alkalies. Made by simply mixing the dry ingredients, it consists of:

Volcanic ash	90 parts
Sodium carbonate	6 parts
Powdered soap	4 parts

Indicative of the old-fashioned sand soaps, which enjoyed popularity for cleaning kitchenware, is a formula given in a British reference text:[22]

Powdered soap	5 parts
Calcined soda	10 parts
Pumice powder	20 parts
Fine sand	65 parts

This may be contrasted with a more modern, well rounded cleaning powder described by Belanger:[23]

Powdered borax	5 parts
Powdered soap	30 parts
Soda ash	5 parts
Powdered volcanic ash	35 parts

The ingredients are mixed intimately by sieving to form a rather versatile general-purpose cleaner and polish with many uses in the kitchen, bathroom, and other parts of the house.

Scouring powders consisting solely of a uniform mixture of soap powder and abrasives make efficient cleansing agents.[24] A typical preparation of this type has been described[25] as consisting of 7% soap powder and 93% powdered silica. Obviously, the proportions of these two ingredients, as well as the type of abrasive used, may be varied to meet specific requirements.

In other instances, the sodium carbonate may be reduced partially or supplemented by the use of other detergent alkalies. In the two formulas following,[26] soda ash is used in conjuncion with trisodium phosphate to make effective household scouring powders:

Ingredient	A	B
Soap powder	2	4
Soda ash	3	13
Trisodium phosphate	40	8
Silica (100–125 mesh)	55	75

[22] G. P. Forrester, *Pharmaceutical Formulas*, Vol. II, 10th ed., London. *Chemist & Druggist, 1934*, 562.

[23] E. Belanger, *Drug and Specialty Formulas*, Chemical Pub. Co., New York, 1941, p. 6.

[24] F. W. Smither, "Washing, Cleaning and Polishing Materials," Natl. Bur. Standards Circular C424, Washington, U. S. Dept. Comm., 1939, pp. 20–21.

[25] H. Bennett, *Chemical Formulary*, Vols. I–VI, Chemical Pub. Co., New York.

[26] Anon.; *Soap & Sanit. Chem., 19*, 30 (April, 1943).

These are all scouring powders. Formula A is very strongly alkaline. For general household use trisodium phosphate may either partly or totally be replaced by tetrasodium pyrophosphate. On the manufacture of the less popular abrasive cleaners in paste form, Lesser has the following to say:

Intended primarily for rough and tough kitchenware cleansing, the study[20] of a few products on the market showed their composition to be within the range of the following figures:

Soap chips (dry)	12–20%
Coarse pumice	30–50
Sodium silicate	2–5
Glycerine	1–5
Water	25–40

Thus, the average composition of one of these scouring pastes is about 18% soap chips, preferably the yellow type, which would approximate 15% anhydrous soap; 40% pumice of a coarse but uniform grade; 3% commercial, 40° Bé sodium silicate (Na_2O : $3SiO_2$); about 35% water; and 2% glycerine. Such pastes are used by rubbing a wet cloth over the surface of the cleanser and then scouring the pot or pan as one would use a metal paste polish.

The method of producing such pastes is along the lines already described. Bennett[25] gives the following representative formula for a cleansing paste:

Powdered hard soap	5 parts
Sodium carbonate	10 parts
Fine pumice powder	60 parts
Sea sand	25 parts
Glycerine (as a 5–10% aqueous solution)	Sufficient to make a paste

It is possible to produce such a paste by first preparing a concentrated hot solution of the soap, then adding the powder ingredients in a strong paste mixer or a kind of paint mill until a stiff paste is formed. The consistency of the paste is regulated by the addition of glycerine water.

It should be mentioned that a number of United States and foreign patents exist for abrasive cleaners. We have confined ourselves here to the description of cleaning compounds unprotected by patent rights.

The choice of abrasive in the above compounds is one of extreme importance in avoiding undue costs and yet giving the abrasiveness desired without scratching. For example, an abrasive used in a wall cleaner must be softer than one used on windows, one for aluminumware softer than one for steelware. Usually the manufacturer employs a compromise type of material. The following materials are listed in order of hardness.[27] Generally, they are used in a size of 200 mesh or finer.

Talc: hydrous magnesium silicate; very soft; suitable for special scouring agents for tile and porcelain enamel, but not for general household powder.

Diatomaceous earth: siliceous skeletons of small aquatic plants called diatoms; also

[27] J. W. McCutcheon, *Chem. Ind.*, 65, No. 5, 748 (1948).

called infusorial earth, kieselguhr, tripolite, etc.; soft; expensive; not recommended in general household product.

Whiting: washed chalk; suitable for tile cleaners, etc. but not for a general household product.

Marble: calcium carbonate; mild abrasive not generally used in household cleaners.

Volcanic ash: sedimentary rock composed of volcanic dust, ash, and cinders; suitable for use in household cleaners. Pumice, also a derivative of volcanic ash, is slightly harder than it.

Feldspar: mixture of various metal aluminum silicates, chiefly $K_2O \cdot Al_2O_3 \cdot 6SiO_2$. Its hardness is just about the equivalent of volcanic ash, and it is usually of a whiter color, so that it is a very desirable product when available.

Quartz: crystallized SiO_2. It is harder than pumice and is apt to be abrasive on softer metals such as aluminum and copper. Not recommended where milder abrasives are available.

Sand: fine grains of disintegrated siliceous rock, chiefly quartz which it resembles in hardness.

In many cases the soap plays a minor role, as noted by the formulas given above. This fact leads to an interesting development, namely, the use of synthetic detergents to replace soap in the formula. A product containing 5% soap will rapidly lose its sudsing value through precipitation of the soap by the hard water. This destroys the penetrating action necessary to such cleaners. Synthetic detergents which are not affected by hard water retain this property under all conditions of use and in America have largely captured this type of market.

A very important group of abrasive cleaners are the *hand cleaners* for mechanics, garage workers, and other industrial workers. *Federal Specification* PD-221 is quoted as an example of a hand cleaner.

Detergent for mechanics use shall be of one type only. It shall be a uniform mixture in powder form, as specified, and shall be satisfactory for removing oil, grease, paint, printing inks, and other occupational soil from the hands of automobile mechanics, machinists, and other operatives without harmful effect on the skin. [This last phrase is most important and will be discussed at some length later on.]

The material shall be a uniform, free-flowing powder. The odor shall not be objectionable; if desired, shall conform to the odor of a sample mutually agreed upon by buyer and seller. The mutually agreed upon sample shall be kept in an airtight, closed container for comparison with samples from deliveries. Volatile matter at 105 to 110°C. shall not exceed 5%. Deliveries which yield more than 5% of volatile matter shall be rejected without further test. Alkaline salts, calculated as sodium carbonate (Na_2CO_3), shall be not less than 2% nor more than 5%. The alkaline salts shall consist of borax, sodium carbonate, or a mixture thereof. Free alkali, calculated as sodium hydroxide (NaOH), shall not exceed 0.1%. Free acid, calculated as oleic acid, shall not exceed 0.2%. Anhydrous soap, calculated as soda soap, shall be not less than 17%. Insoluble siliceous matter shall be not less than 60% nor more than 76% and shall conform to the following requirements:

Retained on:

No. 60 sieve	5% (max.)
No. 100 sieve	30% (max.)
No. 200 sieve	60% (max.)

Rosin or sugar shall not be present. Total glycerol contents shall not exceed 0.8% of the weight of the anhydrous soap contained in this product. All constituents shall be reported on the basis of the sample as received, except glycerol which shall be determined on the basis of the anhydrous soap content.

More recently a revised specification (PD-221a) was published. The new specification differs from PD-221 in that a third type of detergent is specified as open for bidding. Type III is a hand scouring powder with vegetable abrasive. This detergent for mechanics' use "shall be a uniform mixture in powder form of clean sawdust or cornmeal, thoroughly saponified soap, and/or active, salt-free synthetic detergents, and pine oil. The detergent shall not contain any mineral abrasives, such as lava, pumice, sand, quartz, etc. Sawdust, if used, shall be of a granular nature and free from splinters." Detailed requirements of type III are: matter volatile at 105°C. —10%; alkaline salts (as sodium carbonate)—0.2%; free alkali (as sodium hydroxide)—0.1%; free acid (as oleic)—0.5%; matter insoluble in water (sawdust or cornmeal)—62%; rosin—5%; sugar—none; volatile hydrocarbons—5%. All constituents must be reported on the basis of the sample as received.

It is interesting to note that cleaners are specified which contain vegetable abrasives. For this purpose corn meal, etc. are chiefly used, since these kinds of abrasives are less irritating to the skin than the common mineral abrasives mentioned under scouring powders.

Since the bulk of these products go to industrial workers, a great many specify the use of abrasives with a vegetable origin. Cornmeal is by far the greatest single material used and its preparation for this purpose usually involves degermination to insure its keeping properties. Undegerminated cornmeal has the annoying property of becoming moldy and wormy. Wood flour is also used. The general consensus among industrialists is that the use of nonabrasive materials is insurance against skin infections that might be caused or aggravated by a mineral abrasive. The great drawback to such materials, however, is their bulkiness and habit of clogging drains. In many applications, however, mineral abrasives are desirable for their greater abrasive power and are used where the individual or company assumes responsibility for any infections derived therefrom. Particularly, mineral abrasives are used in paste soaps for mechanics where the more elaborate powder dispensers would be an inconvenience.

The manufacture of abrasive hand cleaner is similar to other abrasive cleaners. The following formulas may serve as a basis,

A *mechanics' soap* in paste form may be produced from: 130 parts transparent soft soap, 150 parts bentonite, 200 parts fine sand, 10 parts sodium carbonate. The solid materials are incorporated into the soft soap. Some water may be added to regulate consistency.

A *hand cleaner in powder form* may be produced by the following basic formula: 26 parts pure powdered soap, 70 parts abrasive material (corresponding to the requirements of U. S. Federal Specification PD-221 or PD-221a), 4 parts of borax and/or sodium carbonate.

A special *hand cleaning compound containing approximately 75% of borax and 25%* of dry soap was found in the laboratories of Borax Consolidated Ltd. to possess desirable fungicidal properties and yet to be so mild in its action on the skin as to reduce any tendency to dermatitis. The borax is in finely granulated form so that, when mixed with dry powdered soap, gumming or caking is avoided. The product is described as a good cleaner and will remove dirt from the hands effectively and without waste. The borax is added not just as a diluent for the soap, but its hardness of 2 (in the hardness scale) makes it softer even than chalk; it is readily soluble, and its abrasive action is only temporary, as the sharp edges of the grains become blunted almost instantly. It has detergent and slight water softening properties of its own, and is a mild alkaline salt possessing the characteristic properties of imparting to a soap solution a pH value lower than soap alone.[28]

Grit soaps in cake form are popular as well. It is possible to produce such a soap simply by incorporating the abrasive material into the hot soap in the crutcher. Suitable for this purpose are soaps (not grained-out) produced from coconut oil or palm kernel oil, as they foam better and the incorporation of the abrasives is easier because the soaps remain liquid, or at least movable, in the crutcher even if higher amounts of insoluble material are added. The soap is adjusted to a fatty acid content of 60% before the abrasives are added in the crutcher, or in a small soap pan fitted with a strong stirring mechanism. The production of the soap base may be carried out by the boiling method or the semiboiled process. Fatty acids may be used to great advantage. The abrasives are slowly added to the hot soap base with constant stirring. The soap–abrasive mixture is poured into frames, and is cut after it has solidified. Some representative formulas for grit soaps in cake form are as follows; 75 parts soap base, 5 parts sodium silicate (40° Bé), 10 parts pumice, 10 parts fine sand (or 5 parts bentonite, 5 parts kieselguhr, and 10 parts pumice, which gives a soap with less scrubbing effect, but more suitable for sensitive skin).

Some of the mineral abrasives may be replaced by vegetable abrasives. If the soap is to be perfumed or colored, the coloring and perfuming ingredients are added to the soap before incorporating the abrasives. It is sometimes suitable to mix ultramarine with the abrasive to cover the greyish appearance of most of the abrasive materials. 0.5–0.75%, calculated on the pan soap, may suitably be used.

The use of bentonite (see Chap. IX, 8) in products as prescribed in the

[28] Anon., *Chem. Eng. News,* 21, 1753–1754 (1943).

above specification and specimen formulas has many advantages. Bentonite appears to be without harmful effect on the skin. This is demonstrated by the fact that bentonite is even used as an ointment base for dermatological conditions. Because of its colloidal properties it does not cause clogging of plumbing, which is especially important when industrial hand cleaners are used regularly. Lesser,[29] in a review on the use of bentonite as a detergent, mentions particularly its use for industrial hand cleaners.

In the cleaner developed and recommended by the U. S. Public Health Service[30] to meet its own rigid requirements and standards, bentonite was advocated as one of the two alternate colloidal clays useful in such products, the other being kieselguhr. These colloidal clays, it was noted, provided good detergent action, acted as soft scrubbers, had no skin-irritating properties, and caused no clogging of plumbing. The type of formula for such an industrial cleanser for general use was given as follows:

Neutral toilet soap	30 parts
Colloidal clay (bentonite or kieselguhr)	30 parts
Synthetic detergent	10 parts
Lanolin	5 parts
Perfume	1 part

Mix the colloidal clay and synthetic detergent. Heat the soap and lanolin and mix with the above. This may be pressed into cake form, or 25 parts of corn meal may be added to make up 100 parts and the mixture then made into a powdered soap.

It may be significant that only bentonite was mentioned when this formula was included among those recommended by the Committee on Occupational Dermatoses of the American Medical Association.[31]

It is also possible to add to a soap base not only abrasive but also *solvents*. Such soaps are especially suitable for hand cleaning soaps for workers in the paint and dyestuff industry,[32] but only with 10–15% of solvents and only abrasives of the softest type (*e.g.*, bentonite, saw dust, etc.) to prevent the solvent from entering into skin scratches produced by harder abrasives. Solvents may be added to hand cleaners in paste or cake form. Only higher boiling solvents with no irritating effect should be used, *e.g.*, deodorized kerosene or refined solar oil (or light mineral oil). No chlorinated or low-boiling solvents should be employed, although cleaners' naphtha is permitted. Some formulas for abrasive hand cleaners containing solvents are:

SOAP IN CAKE FORM

70 parts of hot liquid curd soap
20 parts bentonite and/or sawdust
10 parts solvent (solvents as mentioned above)

[29] M. A. Lesser, *Soap*, *21*, No. 10, 39 (1945).

[30] L. Schwartz, *Med. Clin. N. Am.*, *26*, 1195 (1942); *Ind. Nursing*, *4*, 36 (April, 1945).

[31] Committee on Occupational Dermatoses, *J. Am. Med. Assoc.*, *122*, 370 (1943).

[32] J. and A. Davidsohn, *Soap, Perfumery & Cosmetics*, *15*, 382 (1942).

SOAP IN PASTE FORM

60 parts soft soap
15 parts solvent (see above)
25 parts bentonite and/or sawdust

If the paste is too stiff, water may be added. First the solvent is added to the soap and then the abrasive is incorporated slowly until a smooth paste has been formed.

(4) Salt Water Soaps

Salt water soaps are important and it is imperative that the soap manufacturer be well acquainted with their composition and the requirements prescribed for the U. S. Navy—the largest consumer of this type of soap. The main constituent of the fat charge of the classical type of salt water soap is coconut oil or palm kernel oil, owing to the greater electrolyte resistance of

TABLE XX-4

COMPOSITION OF SALT WATER SOAP ACCORDING TO FEDERAL SPECIFICATION PS-611a

Constituent	Percentage by weight	
	Max.	Min.
Anhydrous, salt-free, soap	—	40.0
Moisture and matter volatile at 105°C.	55.0	—
Free alkali, calc. as NaOH	0.5	—
Chloride calc. as NaCl	3.0	2.5
Matter insol. in distilled water	0.5	—
Acid number of mixed fatty acids prepared from soap	—	240
Sugar and foreign matter	None	None
Rosin	None	None

this type of soap, the faster solubility in cold salt water, and the greater lime resistance. The acid number (neutralization value) of the mixed fatty acids separated from salt water soaps should be 240 according to Federal Specification PS-611a (see Table XX-4), which means that about 75% of the fats used must be coconut, palm kernel, or babassu kernel oil. Owing to the scarcity of these oils it was found necessary to modify the specification, and toward the end of 1942 the Navy Department issued an Interim Specification (51-D7), which prescribed a compound bar soap containing soap in conjunction with synthetic detergents preferably of the aryl alkyl sulfonate type (see Table XX-5).

The physical chemistry of the functioning of this mixture in sea water is a controversial subject. Van Zile and Borglin[33] give the following opinions as prevalent among workers in this field. Some believe that in the presence

[33] B. S. Van Zile and J. N. Borglin, *Oil & Soap*, 21, 164–166 (1944).

of hardness, soap and a synthetic detergent form a complex perhaps of the nature:

$$
\text{Ca} \begin{cases} \text{soap} \\ \text{synthetic} \end{cases}
$$
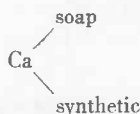
This complex not only acts as a precipitant for hardness, but, having greater solubility than the calcium soaps, aids in dispersing the insoluble curd. When the hardness has all been precipitated and dispersed, sufficient synthetic will be left to aid the soap in doing a wash job. Others feel that the soap alone precipitates the hardness and the synthetic does the washing. If this is the case the soap is wasted, because the synthetic could be used alone and should do just as good a job without softening the water. Another school of thought is that the soap precipitates the hardness; the synthetic then disperses

TABLE XX-5

Composition According to Navy Interim Specification 51-D7

Constituent	Percentage by weight	
	Max.	Min.
Anhydrous, salt-free, soda soap	—	30
Anhydrous, salt-free, synthetic detergent	—	20
Moisture and matter volatile at 105°C.	25	—
Free alkali, calc. as NaOH	0.1	—
Matter insol. in distilled water	0.1	—
Rosin	4.0	—
Sugar	None	None
Sodium sulfate, sodium chloride and other neutral inorg. salts	Balance	Balance

the insoluble soap and allows the excess soap to do the actual washing. Whatever the physico-chemical mechanism, the fact remains that the combination of soap and synthetic works better than either one alone. Also, the combination works at a relatively low concentration, which seems to rule out any thought of the complete precipitation of the hardness.

It is interesting that the use of rosin is excluded in Federal Specification PS-611a and in a similar specification issued by the American Society for Testing Materials (A. S. T. M.) (D593-42) adopted 1942 and maintained until now. The Navy's Interim Specification permitted the use of 4% rosin (calculated on the weight of the compound soap). The soap must be made chiefly from tallow but may contain 10% of other fats or oils, or rosin. It should be a boiled settled soap.

Extensive research was carried out by Van Zile and Borglin,[33] who proved the value of rosin in sea water soaps, especially in conjunction with tallow

soaps and alkaline soap builders. Their experiment to prove the detergent value of these soaps were carried out according to the performance test as outlined in the Navy Interim Specification 51-D7, which is briefly as follows:

Wool fabric is soiled by passing through a soiling solution a sufficient number of times to reduce the reflectance to 30% ($\pm$ 2.5%). The soiling solution is composed of:

Edible tallow	2.5 g.
White mineral oil	6.0 g.
Lampblack (Grinder No. 2)	0.125 g.
Carbon tetrachloride	4.0 l.

After soiling, the wool fabric is washed by the following procedure. Dissolve the sample in 1000 ml. of artificial sea water, warming if necessary. Take 250 ml. of this solution in an 8 in. evaporating dish and wash a 4 in. square piece of the soiled wool fabric by squeezing it vigorously 50 times in the detergent solution within two minutes. Rinse in warm soft water and dry. The reflectance is then compared with that of an unsoiled piece of the wool fabric which has been squeezed 50 times in artificial sea water, rinsed and dried.

The composition of the artificial sea water is:

Magnesium chloride ($MgCl_2 \cdot 6H_2O$)	11.0 g.
Calcium chloride ($CaCl_2 \cdot 2H_2O$)	1.6 g.
Sodium sulfate (Na_2SO_4)	4.0 g.
Sodium chloride (NaCl)	25.0 g.
Water to make	1.0 l.

The concentration of detergent used in this test was varied until a solution was obtained which would remove all of the visible black from the wool fabric. The lowest concentration that would accomplish this was considered the optimum for the detergent. Coconut oil salt water soap (PS-611a) required 7% of dry solids, or over 15% on the 55% moisture basis. The addition of alkaline builders reduces the necessary concentration. Mixtures of 50 parts of soap with 50 parts of trisodium phosphate, metasilicate, orthosilicate or soda ash required about 6%, while a 50 : 50 mixture of soap and tetrasodium pyrophosphate required only 4.75%.

For salt water use sodium resinate alone aids soap very little, but combined with alkaline soapbuilders it is very effective. For instance, it requires only 3% of a mixture of 50% tallow soap, 25% resinate, and 25% pyrophosphate to meet the above test. The soap containing synthetic detergent as specified in 51-D7 requires between 2.0 and 2.5% to do the same thing. By using a slightly higher concentration, Van Zile and Borglin succeeded in obtaining a good detergent for use in sea water without the use of synthetics.

A formula by Young et al.[34] uses the rosin acids of tall oil as a base in which the potash soap is mixed with the sodium salts of the builders:

[34] C. B. F. Young et al., *Soap & Sanit. Chem.*, 25, No. 12, 42 (1949).

SCRUB SOAP—USING TALL OIL

Tall oil potash soap	30
Sodium carbonate	4
Pine oil	7
Trisodium phosphate	4
Water	55

Since a mixture of one part of tallow soap and one part of pyrophosphate required a concentration of 4.75% to remove all of the visible carbon black, it was endeavored to reduce the necessary concentration through the addition of sodium resinate. Starting with a 50 : 50 mixture of detergent and builder, sodium resinate was added in increments of 5% from 5 to 30% and the pyrophosphate was reduced by a like amount. The best protection was obtained with 50% tallow soap, 25% resinate, and 25% tetrasodium pyrophosphate mixture. Working from the other angle, a mixture of 2 parts tallow soap to 1 part of resinate was used, and pyrophosphate was added in increments of 5% from 5 to 25%, decreasing the amount of soap resinate mixture to the same extent. The pH was 9.5, corresponding to a pH of a 3% concentration of the salt water soap in artificial sea water. If the pH was raised to 11.0, better results were obtained. These can be obtained by finishing the soap at a slightly higher alkalinity. It was found that the most effective composition was 2 parts of tallow soap to 1 part of resinate and 1 part of alkali salts (part of which must be tetrasodium pyrophosphate). Of the alkaline salts, it was found that 50 to 60% could be metasilicate, orthosilicate, or trisodium phosphate, with the balance tetrasodium pyrophosphate.

The soap used in this work was a 25° titer soap produced by Colgate-Palmolive-Peet under the trade name Arctic Crystal. The sodium resinate was a spray-dried material made by the saponification of refined wood rosin and sold under the trade name Dresinate.[35] The alkaline salts were the usual grade used in soap production.

[35] Hercules Powder Company, Wilmington, Delaware.

SPECIAL SOAPS

(1) Liquid Soaps

In this section only the common liquid soaps are described. For liquid shampoos and liquid solvent soap, see Chapter XX and Section 4 of this chapter.

Liquid laundry soaps are produced from cheap raw materials without the addition of perfumes or only with the most inexpensive types of perfumes. Liquid toilet soaps are manufactured by the same method, but very often contain additions of glycerine, alcohol, etc. and are more carefully prepared. The limits for free alkali are lower and more closely controlled.

Liquid soaps usually are water solutions of a neutral potash soap, mainly from coconut oil. Sometimes the coconut oil is partly replaced by palm kernel oil, olive oil, peanut oil, and other vegetable oils. The use of fats with high titer are out of the question, as their solution would become thick and turbid. The concentrated soap before dilution with distilled or deionized water is usually prepared by the cold or semiboiled process.

The formulas which follow are suitable for laundries and, when perfumed, for dispensing and automatic machines. Their manufacture is a simple matter.

(a) 250 kg. palm kernel oil, 50 kg. castor oil, 140–145 kg. caustic potash (50° Bé), 800 kg. water; 50 kg. glycerine (28° Bé).

(b) 200 kg. coconut oil, 50 kg. castor oil, 120–125 kg. caustic potash (50° Bé), 800 kg. water; 160 kg. potassium chloride solution (5° Bé).

(c) 100 kg. coconut oil, 60 kg. sunflower oil, 30 kg. castor oil, about 85 kg. caustic potash (50° Bé), 100 kg. glycerine, 535 kg. potassium carbonate solution (5° Bé), 500 kg. water. (This formula is suitable only for laundries.)

To manufacture these soaps by the semiboiled method, the fat is melted and transferred to the kettle (through a fine sieve or cloth if necessary), so that the ready saponified concentrated soap before dilution contains about 40–50% acids. The caustic potash and all filler solutions for liquid soap

manufacture should be well clarified by settling. The potash lye, part of the water, and the glycerine at a temperature of about 75°C. are then stirred in, with continued stirring until combination and heat evolution commence and a thick soap appears in the kettle. The latter is tested for free alkali with phenolphthalein. A cloudy appearance of a sample dissolved in distilled water indicates the presence of unsaponified fat.

The remaining portions of water and filler solutions are then stirred in, preferably at an elevated temperature. The kettle is covered again and the soap mass allowed to stand without agitation. It should be perfectly transparent. Cooling is to about 50°C., followed by filtering and drumming.

The kettle for this process is usually steam-jacketed and includes an efficient stirring device, which should be constructed so that it remains below

TABLE XXI-1

Fatty Acid Content, %	15	25	35
Coconut oil	10.75	16.75	10
Olein (red oil)	5	5	8
Olive oil	—	5	—
Palm kernel oil	—	—	11.5
Castor oil	—	—	7
Caustic potash lye	14.5 (30° Bé)	13 (40° Bé)	18 (40° Bé)
Potassium carbonate	1	0.5	0.5
Potassium chloride	1	—	—
Alcohol	—	4.5	10
Sugar	5	7.5	6
Glycerine	—	7.5	5.5
Distilled (or deionized) water	62.75	40.25	31

the surface of the liquid at all times in order to avoid beating air into the mixture.

Formulas for liquid soaps with different fatty acid contents are given in Table XXI-1. The rather old fashioned use of sugar may be replaced by use of other thickening agents of modern type, such as methylcellulose, sodium carboxy methylcellulose, etc. and not in such high percentages; the difference to 100 may then be made up by more water and/or glycerine.

If the saponification is carried out at the boiling point the whole of the fat stock is run into the soap pan with half its weight of water and heated by steam. The saponification process is carried out as usual. Full saponification assured and free alkali adjusted, the ready boiled soap may be diluted suitably, after the soap has remained at rest for some hours to prevent foaming during the dilution process. Thickening agents and emulsifiers, if any,

are added during the last stage of dilution. They are dissolved previously in some of the distilled water.

Table XXI-2 for liquid soaps of different composition is taken from an article by Oculus.[36] These may be compared with the series (Table XXI-3) which incorporate small proportions of linseed oil or soybean oil.

Another method of producing liquid soaps is to dissolve flakes of previously prepared cold-made potash soap from coconut or palm kernel oils in water. To produce a potash soap of 56–57% fatty acids content, the following formulas may be used: (a) 60 parts coconut oil, 31.3 parts KOH

TABLE XXI-2[36]

Fatty acid content. %	10	12	15	20
Coconut or palm kernel oil, kg.	10.5	12.6	15.75	21.0
Potash lye (50° Bé) (approx.), kg.	5.4	6.5	8.1	10.8
Water (with the addition, if needed, of 0.5% KCl), kg.	78.0	76.0	75.0	66.0
"Strengthening" agent (i.e., emulsifying and wetting agent) of the turkey red oil type, kg.	1.2	1.2	1.5	2.0
Thickening agent (sugar, gums, Carbowaxes, etc.) (approx.), kg.	1.5	1.5	—	—

(50%), to which 10.0 parts water was added previously; (b) 60 parts palm kernel oil, 30.7 parts KOH (50%), to which 10.0 parts water was added previously. The soap is produced as described in the chapter on cold-made soaps (Chapter XIX). After the soap has saponified completely in the frames, it is flaked and kept in closed containers.

TABLE XXI-3

Fatty acid content, %	10	12	15	20
Coconut oil or palm kernel oil, kg.	6.5	8.0	10.0	14.0
Linseed or soybean oil, kg.	4.0	4.6	5.75	7.0
Potash lye (50° Bé) (approx.), kg.	5.0	6.0	7.45	10.0
Water (with addition, if required, of 0.5% KCl), kg.	82.0	79.0	76.0	67.0
Strengthening agent, kg.	1.0	1.2	1.5	2.0
Thickening agent (approx.), kg.	1.5	1.0	—	—

When used for liquid soaps the potash soap flakes are dissolved in a suitable amount of water, with the addition of 0.5% potassium chloride as described for dissolving soft soaps. The following formula gives the amount of soap with different fatty acid content to be dissolved in distilled or deionized water to produce 100 parts liquid soap:

$$c = b/a \times 100$$

where a = fatty acid content of soap concentrate, b = fatty acid content of liquid soap aimed at, and c = parts of soap concentrate to be dissolved.

[36] Oculus, *Seifensieder Ztg.*, **63**, 696 (1936).

It is possible to prepare cheap liquid soaps from common transparent soft soap (see Chapter XIX-3), especially if the soft soap for this purpose does not contain additions of salts (soda ash, etc.). To prepare a liquid soap with 15% fatty acid content: 37 parts of transparent soft soap with 40% fatty acid is dissolved in 63 parts of distilled or deionized water, with the addition of 1–2% "strengthening" agent, *e.g.*, turkey red oil (clearly soluble in water) or a non-ionic detergent.

The ready-made soft soap, most suitably a soap from a fat charge containing some 10–15% coconut oil, is dissolved in one-third of the water and heated. After the soap has been completely dissolved, the remainder of the water is added.

TABLE XXI-4[37]

Test	Liquid polyethylene glycols of mol. wt.:			
	200	300	400	600
Freezing range, °C.	Supercools	− 15 to 8	7–10	20–25
Sp. gr. at 20/20°C.	1.12	1.13	1.13	1.13
Flash point, °F.	350	385	435	> 450
Saybolt viscosity at 210°F., sec.	38–41	42–46	45–55	60–70
Water soly. at 20°C., by wt.	Complete	Complete	Complete	Complete
Comparative hygroscopicity, glycol = 100	90	70	60	50

Test	Carbowax compounds of mol. wt.:				
	1000	1500	1540	4000	6000
Freezing range, °C.	35–40	35–40	40–45	50–55	58–62
Sp. gr. at 20/20°C.	—	1.15	1.15	1.2	—
Flash point, °F.	> 450	430	> 450	> 475	> 475
Saybolt viscosity at 210°F., sec.	80–100	60–90	100–150	500–700	6000–7500
Water soly. at 20°C., by wt.	70	73	70	62	approx. 50
Comparative hygroscopicity, glycol = 100	5	30	5	1	.1

Of interest here as thickening agents are the Carbowaxes.[37] These are polyhydroxy ethylene glycols of general formula $CH_2OH(CH_2OCH_2)_x$—CH_2OH. The Carbowaxes comprise a series of products that include both liquids and waxlike solids, as can be seen from the data in Table XXI-4. All are unctuous but water soluble—a combination of properties long desired for many applications in industry. It is easy to understand that these compounds are valuable additives for textile soaps and they may also prove to be of value for toilet soaps.

Other thickening agents are solutions of methylcellulose, sodium carboxymethylcellulose (C.M.C.), etc. Other additions to liquid soap are listed in the chapter on shampoos (Section 4).

[37] Carbide and Carbon Chemical Corp., New York.

It is also possible to thicken liquid soaps with inorganic salts such as KCl, potassium acetate in 1–2% addition[38] or even by the use of sodium salts such as trisodium phosphate or better tetrasodium pyrophosphate and sodium tripolyphosphate. In the latter case, the production of the more insoluble sodium soap by ion exchange may be partly responsible for the thickening.

The addition of perfumes to liquid soaps should be carried out at low temperature. The usual perfumes for soap perfuming are suitable for liquid soaps as well. An addition of alcohol (ethyl or propyl alcohols) to the liquid soap makes it possible to dissolve the perfumes in the whole amount of alcohol to be used before adding it to the soap. Alcohol has the advantage of increasing the solubility of the soaps, thus helping to keep the liquid soap
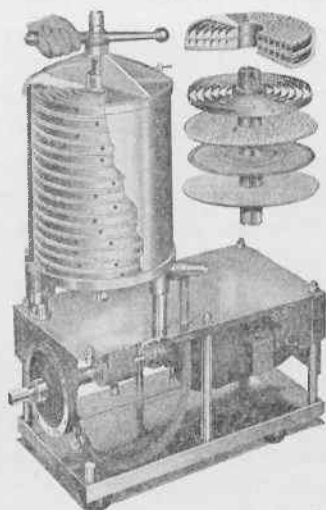
Fig. XXI-1. Portable filter and pump unit (courtesy Alsop Engineering Corporation).

clear. For this reason, percentages of alcohol added are lower for low concentration liquid soaps and higher for higher concentration soaps. The percentages range from 2% for liquid soaps with 15% fatty acid content up to 10% for soaps with 35% fatty acid content. In case additions of glycerine are made, the percentage of alcohol may be considerably lowered.

A very important problem faces every manufacturer of liquid soaps—the clarification of his product. The public prefers a clear, sediment-free liquid soap, and the manufacturer must keep this in mind before putting his product on the market. The surest method of clarification is to use a refrigeration unit which brings down the temperature of the soap to 5°C. or even below and then to filter the cold soap through a filter press or disc filter, eventually using a filter aid of the kieselguhr type or alumina. Fig. XXI-1 shows a mul-

[38] *Alchemist*, 4, No. 9, 217–221 (1950).

tiple-disc drum filter. These machines are produced in different sizes. Maximum pressure is 30 p.s.i.

Other methods include cooling inside cold rooms at temperatures as low as possible, but above 0°C., and filtering in the cold room with the help of a filter aid through suitable cloth.

In order to keep the liquid soap clear until it is consumed, the following conditions should be met: (1) the containers should be clean, (2) there should be no unsaponified fat, (3) there should be some small percentage of free alkali (0.02%, but not exceeding 0.05% free KOH) and (4) filtering should have been carried out in the cold. A small percentage of a suitable non-ionic detergent also often helps to prevent cloudiness.

Liquid soaps are liable to attack to a very slight degree the glass containers in which they are kept, which often creates a cloudy appearance after several months' storage of an originally brilliantly clear solution. The addition of certain sequestering agents which form complexes with these siliceous materials is very helpful and prevents this condition.[38a] The best known agent is ethylenediamine tetrasodium acetate, variously known as Sequestrene, Nullapon, Versene, etc. A few tenths per cent is all that is required. A recent patent[38b] covers a similar type of product. Sodium tetrapyrophosphate has also been used for this purpose, but with less permanent effect.

To prevent cloudiness resulting from the storage of alkaline liquid soaps in glass containers, U. S. Patent 2,402,557 by Kranich (1946) prescribes the addition of 0.07–2% of commercial sodium silicate to the liquid soap, heating to 70°C., allowing to stand for a week, cooling to 4°C. and filtering. The resulting liquid soap contains traces of silica in a soluble form which prevent the attack on the glass by the liquid soap.

When perfuming liquid soaps, care must be taken to choose a perfume material that does not deteriorate under alkaline conditions prevailing in liquid soaps. Perfumes containing terpenes should be avoided as well as alkaline-sensitive types of perfumes and aromatic chemicals. Many aldehydes are also unsuitable for perfuming liquid soaps, since polymerization may occur under alkaline conditions, giving rise to turbidity and discoloration (e.g., vanillin). Schwarcz[39] enumerates some perfumes which are suitable for liquid soaps. They are geranium, patchouli, petitgrain, rosemary, spearmint, and bois de rose (see Chapter XXV). Some perfume formulas will be found in the chapter on shampoos (Chapter XXI).

Norwood[40] gives an unusual liquid soap formula which may be used in

[38a] H. Kranich, *Soap & Sanit. Chem.*, 23, No. 11, 33–35 (1947).

[38b] F. C. Bersworth, U. S. Pats. 2,461,519 and 2,524,218.

[39] L. Schwarcz, *Sanitary Products*, McNair-Dorland, New York, 1943, p. 96.

[40] W. D. Norwood, *Indus. Med.*, 39, 253–267 (Feb., 1939).

munition factories to indicate the presence of T. N. T. or tetryl on the hands, which may easily cause dermatitis. In the presence of these materials the potassium sulfate causes the soap to show a purple color.

Liquid soap	90–75%
Potassium sulfate	5–10%
Wetting agent	5–15%

The following specifications are of interest.

(a) Federal specification PS-586: Liquid Laundry Soap.
Liquid soap for laundry use shall be a clear solution of pure potash (or potash and soda) soap with or without glycerol or alcohol and containing not less than 12% by weight of a volatile organic solvent or a mixture of such solvents. It shall yield a clear solution on mixing with soft water, shall quickly form a satisfactory lather, shall have no injurious effect, and leave no objectionable odor on fabrics. Materials washed with this soap shall have, after drying, a soft feel and not appear more boardy or stiff than when washed with soft water.

The material shall be a clear solution, shall yield a clear, homogeneous solution on mixing with soft water, shall quickly form a satisfactory lather, and shall leave no objectionable odor on fabrics. Total anhydrous soap shall be not less than the equivalent of 24% potash soap. Total matter insoluble in alcohol shall not exceed 0.5%. Free alkali, calculated as potassium hydroxide (KOH), shall not exceed 0.05%. Chloride, calculated as potassium chloride (KCl) shall not exceed 0.3%. Total matter insoluble in water shall not exceed 0.1%. Volatile organic solvent shall be not less than 12%. All constituents shall be calculated on the basis of the original sample. Fabric washed with the liquid soap shall show no more shrinkage or felting than occurs with similar fabric washed with soft water at the same temperature. Colored materials when washed with this soap shall not fade more than when washed the same number of times at the same temperature with soft water alone.

It is interesting to note here that addition of at least 12% of organic volatile solvent is prescribed (see chapter on solvent soaps, Chapter XX).

(b) Federal specification PS-618: Liquid Toilet Soap.
Liquid toilet soap shall be a clear solution of pure vegetable oil potash (or potash and soda) soap with or without glycerol or alcohol, suitably perfumed, and free from all foreign matter. It shall quickly form a satisfactory lather and have no objectionable odor on the skin. The odor shall not be objectionable in the soap as received or in a hot solution of the soap in water. The material shall not leave any objectionable odor on the skin or other surfaces after washing with a water solution of the soap and rinsing thoroughly with plain water. Unless otherwise specified, each bidder shall submit with his proposal a one-quart sample, placed in a screw-top glass jar, to show odor, color, and consistency. The sample so furnished shall be kept for comparison with samples from deliveries.

The material shall be a clear solution, free from objectionable odor, other than from coconut oil, and shall form a satisfactory lather. Total anhydrous soap shall be not less than the equivalent of 15% potash soap. Total matter insoluble in alcohol shall not exceed 0.5%. Free alkali calculated as potassium hydroxide (KOH) shall not exceed 0.5%. Chloride calculated as potassium chloride (KCl) shall not exceed 0.3%. More than traces of sulfates and sugar shall not be present. All constituents shall be calculated on the basis of the original sample.

(c) A.S.T.M. Standard Specification D799-45 (1945) for *Liquid Toilet Soap* gives the following requirements:

Liquid toilet soap shall be a clear solution of pure vegetable oil, potash (or potash and soda) soap, with or without glycerol or alcohol, free from objectionable odor, and shall form a satisfactory lather. It may be mildly perfumed. The odor shall not be objectionable in the soap as received, or in a hot solution of the soap in water. The material shall not leave any objectionable odor on the skin or other surfaces, after washing with a water solution of the soap and rinsing thoroughly with plain water.

Chemical Composition

Liquid toilet soap shall conform to the requirements as to chemical composition prescribed. All constituents shall be calculated on the basis of the soap as received.

Total anhydrous soap, calc. as potash soap, min., %	15
Matter insol. in alcohol, max., %	0.4
Free alkali, calc. as KOH, max., %	0.05
Chloride, calc. as KCl, max., %	0.3
Sulfates, max.	Trace
Sugar, max.	Trace

The material shall be purchased by a net volume of soap as received. One gallon of liquid soap is equal to 231 cu. in. at $15.5°C.$ ($60°F.$).

The material shall be sampled and analyzed in accordance with the *Standard Methods of Sampling and Chemical Analysis of Soaps and Soap Products* (A.S.T.M. Designation D-460). The purchaser reserves the right to use any additional available information to ascertain whether the material conforms to these specifications.

(d) The *British Soap Makers' Association* has published the following specifications for liquid toilet soap sent for consideration to the British Standards Institution.[41] (We quote only the specifications and not the method of analysis.)

General purpose liquid toilet soap shall consist of an aqueous solution of potassium and/or sodium soap made from vegetable oils. It shall be in the form of a clear solution at $5°C.$, shall show no signs of separation, and shall be free from foreign matter and impurities.

It may be supplied perfumed, but if unperfumed shall have no fatty or disagreeable odor. A suitable dyestuff may be used.

Samples taken at random must comply with the following additional regulations: (a) When tested by the method given below, the material must contain not less than 15% by weight fatty acids. (b) The degree of alkalinity should not exceed 0.04% calculated as potassium monoxide (K_2O). (c) When applied to wet hands the material must form quickly a satisfactory lather. The amount of lather produced by the method described, using a solution consisting of 1 part liquid soap diluted with 5 times its volume of distilled water, shall be not less than 12 times the volume of the solution employed in the tests, and after standing for 5 min. shall not be less than 9 times the volume of the solution employed in the tests. (d) The soap must have no injurious effect on the skin, and must produce no objectionable smell or tacky feeling in use. (e) When stored in its original sealed container under normal conditions for a period of six months, the soap must show no signs of gelling or other deterioration. It must retain its original perfume, if any. (f) There shall be no "seeding out" of solid soap or deposit of solid matter standing for 18 hrs. at $0°C.$

[41] *Manufacturing Chemist*, 14, 323 (1945).

No liquid toilet soap shall be described as "concentrated" unless it contains a minimum of 25% by weight fatty acids.

(2) Transparent Soaps

There was a time when transparent soaps were very popular, especially in Continental countries. Now they have lost much of this popularity and it is often very hard to find a transparent soap in the usual retail stores handling soap products. Still, transparent soaps may regain some of their popularity, especially if there is no shortage of glycerine, sugar, and alcohol, raw materials which are important for their manufacture.

In comparing the value of transparent soaps with ordinary milled toilet soap it must be pointed out that a milled soap has a much higher value than almost any transparent soap. The cost of producing transparent soaps with high fatty acid content is usually much higher than the production costs of a milled toilet soap of similar fatty acid content. In addition, a cake of transparent soap is used up much faster than a cake of milled toilet soap. Still, the eye appeal of transparent soaps remains—a fact not to be overlooked by a soapmaker, especially in times of keen competition. In principle, transparent soaps may be produced from every pure toilet soap by adding a suitable solvent, etc., to produce transparency. For example, if a bar of toilet soap is dried to about 73% fatty acid and dissolved in industrial methylated spirit in a double saucepan over a domestic gas ring until the spirit is boiled off and a small quantity of the soap remains clear and bright when cooled on a watch glass, it may be run into tin molds to produce a very acceptable transparent soap.

On a plant scale, transparent soaps are generally produced by the semi-boiled process. From this fact alone it follows that only pure fats and oils may be used as raw materials to ensure a pure transparent appearance of the finished soap.

Tallow,* bleached palm oil, coconut oil or palm kernel oil, castor oil, and rosin are the most commonly used raw materials for the fat charge. For filling and aids to transparency, sugar, glycerine, and alcohol are the main organic raw materials, and sodium carbonate, potassium carbonate, and sodium silicate represent the main inorganic raw materials. It is of greatest importance that lime should be absent in the raw materials used. (The grade of sugar containing traces of calcium should not be used.) It is also important to use soft water only.

Some formulas for transparent soaps containing *alcohol,* based on neutral fats, follow:

* Tallow may partly or completely be replaced by hardened oils with a similar titer.

	A	B	C	D
Tallow	100	80	40	50
Coconut oil	100	100	40	60
Castor oil	80	80	40	58
Caustic soda 38° Bé	161	133	60	84
Alcohol	50	30	40	30
Glycerine	25	—	20	—
Sugar	80	90	55	35
Dissolved in water	80	80	45	35

Tallow and coconut oil are melted, at 80°C., suitably in a separate container placed over the soap kettle, fitted with a stirrer and run through a filter into the soap kettle. Castor oil is added separately, as it tends to become dark if it is superheated, especially the cruder grades which contain some mucilaginous substances. It is thus suitable to add the castor oil just before the caustic lye is added to the fat charge. The caustic lye mixed with the alcohol is run in a rather strong stream into the fat charge under constant stirring. The presence of the alcohol accelerates the saponification process considerably. Since the kettle is jacketed, the temperature may be regulated in order not to allow the temperature to rise above 75°C. After the saponification is complete (a sample withdrawn is clearly soluble in distilled water), the stirrer is switched off and the kettle left covered for some time. In a separate container or kettle the sugar solution is prepared by dissolving the sugar in warm water at 80°C. Any froth formed at the surface is removed. The next step is to add first to the soap mass in the kettle any glycerine used and then the warm sugar solution. This is carried out under constant stirring. At this stage the free alkali content is adjusted. If it was found too high, coconut fatty acids are added. Roughly every per cent of free NaOH corresponds to 5.3% coconut fatty acids. The free alkali content should not be higher than 0.15% as NaOH. (The Swiss specification permits only 0.1% free NaOH.) Generally, the same procedure should be followed as described for the manufacture of semiboiled soaps. Then the kettle is covered again and left standing until the temperature falls to 60°C., at which point perfume and color solution are added. The color solution is prepared beforehand by dissolving water-soluble color in hot water and filtering through a cloth. After coloring and perfuming, the soap mass is run into frames (see Chapter XIX on semiboiled and cold soaps).

It is possible to produce good transparent soaps from a fat charge containing a high percentage of rosin. Fisher[42] gives the following description for the manufacture of such rosin-containing soaps:

[42] W. J. W. Fisher, *Soap, Perfumery & Cosmetics*, *11*, 520 (1938).

To produce a medium grade of transparent soap the following charge can be used:

	Parts by weight
Tallow	75
Coconut oil	75
Rosin W. W.	50
Caustic soda (37° Bé)	100
Spirit	80
Sugar	40
Water	40

The soap proper may be made either by the semiboiled or the fitted process. If made on the former principle the temperature must be kept as low as possible, and plenty of time given for saponification. When this is complete the sugar solution is added at the same temperature as the soap. When all is added and the soap is thin and free from lumps, the spirit is added, together with any coloring matter. The perfume is incorporated just before running into frames.

If a slightly better soap is required the spirit may be increased, and the sugar and water decreased in the same proportion. There is considerable risk of the soap losing its colloidal state, and crystals may form in the center of the frame if the sugar solution is reduced to below 30 parts in the last charge given, unless the frames are very small or the soap is run into moulds.

Another series of formulas for transparent soap is given by Pfaff:[43]

	A	B	C
Tallow	42	58	34
Coconut oil	42	17	33
Castor oil	10	8	—
Rosin	6	17	33
Caustic soda (38° Bé)	49	47	46
Glycerine	—	25	13.5
Sugar	19.5	—	—
Water	19.5	—	—
Alcohol	42	25	33.5
Approx. yield	*230*	*197*	*193*

It is possible to produce high-grade transparent soaps from fat charges containing a high percentage of stearine as well. Ghose[44] describes the following process for the production of transparent soap withstanding shrinkage and of nonhygroscopic nature:

Stearine	35 parts
Castor oil	25 parts
Coconut oil	40 parts
Caustic soda soln. (37° Bé)	50 parts

[43] K. Pfaff, *Riechstoffind. u. Kosmetik*, **11** (1935).
[44] A. N. Ghose, *Soap, Perfumery and Cosmetics*, **11**, 234–236 (1938).

Sugar soln. 24° Bé	50 parts
Glycerine	30 parts
Alcohol (rec. spirit)	50 parts or more
Spirit-soluble color, if required	q.s.
Suitable perfume	q.s.

Saponification is accomplished with caustic soda. The stearine, oil, etc., are warmed and filtered to·remove suspended impurities. The caustic soda solution is mixed with 15 parts of alcohol and added to the melted oil stock at intervals at a temperature between 60 and 70°C. The vessel is kept on a water bath, where the desired temperature may be maintained during the operation. In order to prevent evaporation of alcohol and other volatile materials, the vessel must have a lid that fits tightly—it being a useful precaution in most cases to wrap a wet rag tightly round the lid to stop any further leakage. The following precautions should be taken, both during saponification and after:

(1) Alcoholic caustic soda should be used for rapid saponification.

(2) The temperature of the hot soap should not exceed 80°C. to 85°C. after the whole of the rectified spirit has been added.

(3) Two hours at least should be allowed for saponification.

(4) The sugar solution and glycerine should be added hot, after saponification.

(5) Color, if added, should be dissolved in some of the alcohol and must be clearly soluble in the latter, leaving no residue. The color solution *must* be filtered before use.

(6) Rapid cooling of the liquid soap (by means of mechanical devices such as a cold-water cooling frame) is essential for maximum transparency.

Ghose gives the following valuable tabulation of difficulties encountered in the preparation of transparent soaps together with suggestions of how to avoid them:

Turbidity. If this occurs, it is due to one of the following causes: (a) incomplete saponification, (b) insufficient alkali—the free oil or fat causing turbidity, (c) incorrect selection of oil stock (if only coconut oil is used, the soap will be turbid).

Opacity. If the soap is insufficiently transparent, besides the above causes, it may be due to one of the following: (a) loss of alcohol by evaporation, (b) insufficient sugar and glycerine, (c) suspended impurities in the raw materials, (d) insoluble color or perfume.

Softness. If the soap is too soft, it may be due to: (a) excess of soft fat, oil, or fatty acid, (b) excess of moisture, (c) insufficient alkali, (d) too little time allowed for saponification.

Alcoholic Odor. Sometimes the soap possesses an unduly strong alcoholic odor which is due to one of the following causes: (a) excessive use of spirit (use less or replace it with glucose, sugar sirup, glycerine, etc.), (b) insufficient fixatives in the spirit (*e.g.*, aromatic gums, balsams and resins, such as gum benzoin, Peru and Tolu balsams, etc.), (c) failure to recover the alcohol after saponification.

The recommended procedure when boiling the soap is to melt the fats and oils on a water bath or in a jacketed pan. The caustic soda solution is mixed with some of the alcohol and slowly poured over the fatty charge. The vessel is then closed and, after ten minutes, the lid is opened, the soap stirred, and the lid replaced. The boiling should take about half an hour longer, after which the rest of the alcohol is added. The heat is then reduced, and the pan allowed to cool, the contents being stirred occasionally, with

due care being taken to avoid the escape of alcoholic vapor. After another half hour, the glycerine, sugar, etc. are added, and the soap is ready. The heat is then completely shut off and the perfume and alcoholic color solution added. It should be noted that some provision must be made for keeping the soap liquor sufficiently warm, as otherwise difficulty will be experienced in pouring it when required. If the liquor is very thick it may be diluted with a little alcohol before pouring.

In a later publication, Ghose[45] gives other compositions for transparent soap (see Table XXI-5).

TABLE XXI-5[45]

Ingredient	I	II
Stearin	40	45
Coconut oil	50	55
Castor oil	5	5
Rosin	5	—
Caustic soda (37° Bé)	50	50
Sugar	20	20
Dissolved in water	10	10
Alcohol	40	35
Glycerine	10	—

We want to point out here, before describing transparent soaps without alcohol, that it is possible to replace some of the ethyl alcohol with isopropyl alcohol and some of the glycerine with glycol and propylene glycol, etc. The addition of Carbowaxes (Carbide & Carbon Chemicals Corporation. See Section 4, this chapter, and Table XXI-4) may improve the quality of the soap and replace some of the sugar.

Some formulas for the production of transparent soaps without alcohol follow:

Formula I. 75 parts high-grade coconut oil, 65 tallow, 55 castor oil, 98 caustic soda (38° Bé), 5 potassium nitrate, 6 soda ash (dissolved in 30 hot water), 65 sugar (dissolved in 65 hot water), 25 filling solution, 40 glycerine. The stock filling solution consists of: 5 parts potassium chloride, 3 potassium carbonate, 2 soda ash, 7 common salt, 68 water.

Formula II. 52 parts tallow, 60 coconut oil, 56 castor oil, 84 caustic soda (38° Bé), 50 sugar (dissolved in 50 hot water), 12 soda ash (dissolved in 40 hot water), 40–80 filling solution prepared from an 8° Bé brine to which potash carbonate is added until it reaches a strength of 12–13° Bé.

The method of manufacture is as follows. In a steam-jacketed kettle fitted with a stirring mechanism the fats are melted and brought to a temperature of 60°C. The steam is shut off and caustic lye is added and then stirred into the fat charge until thickening occurs. Then steam is opened again and the saponification is brought to an end, approximately after 30 60 minutes.

[45] A. N. Ghose, *Indian Soap J.*, 6, 256–258 (1940).

After complete saponification (clear solubility of a withdrawn sample in water) the free alkali content is adjusted as already described with coconut oil fatty acids (0.3–0.4% free NaOH). Then glycerine, the hot sugar solution, and the hot soda ash and potassium nitrate solution are added, and, after the temperature has fallen to about 65°C., the warm (60–65°C.) filling solution. After this, perfume and a clear color solution are added and the soap is run into frames, where it should remain for 6–8 weeks to develop transparency.

It is possible to saponify the fat charge with the caustic lye and to add after complete saponification a previously prepared filling solution, consisting of inorganic salts dissolved in the sugar solution.

Some formulas follow for this method without glycerine:[46]

Formula I. 29 parts tallow, 36 coconut oil, 35 castor oil, 51.5 caustic soda (38° Bé), 92.5 filling solution (consists of 34% sugar, 3.5% soda ash, 2.5% common salt, 1.5% potash, 58.5% water).

Formula II. 53 parts tallow, 34 coconut oil, 31 castor oil, 50 caustic soda (38° Bé), 80 filling solution (consists of 35% sugar, 4% soda ash, 4% potassium nitrate, 3% common salt, 2% potash, 52% water).

TABLE XXI-6[47]

Constituents	Formula	
	I	II
Tallow	60	60
Olive oil	12	12
Coconut oil	18	8
Castor oil	10	10
Caustic soda (38° Bé)	46	46
Palm kernel oil fatty acids	—	10
Glycerine	—	2.5

These transparent soaps are of lower quality and are not to be used for very sensitive skins.

It is possible to produce milled transparent soaps as well. German Patent 574,927 gives the following formulas for such milled soaps:

Formula I. 61 parts tallow, 18 coconut oil, 11 castor oil, 10 rosin, 45.8 caustic soda (38° Bé).

Formula II. 92 parts palm oil, 8 rosin, 42.9 caustic soda (38° Bé).

The hot soap is chilled in a thin layer over rolls and then plodded. The temperature falls from 90–100°C. to about 20°C. in about 2–3 seconds. Thus, the soap layer on the chilling rolls must be very thin.

Other formulas for milled transparent soaps based on a similar process are given by Bennett[47] in Table XXI-6.

[46] Oculus, *Seifensieder Ztg.*, 63, 97 (1936).
[47] H. Bennett, *Formulas for Profit*, World Pub. Co., New York, 1939, p. 484.

On the basis of transparent soaps it is possible to produce specialities of a different kind. If the warm soap is poured from the kettle into small molds of the size of the finished soap cake it is possible to insert in the mold toys, name plates, etc. Any printing on the plate must be done with alkali-resisting printing ink. This is a somewhat complicated procedure and only feasible when a good price can be obtained for such specialities. The same applies to the method described by Ghose[48] for inserting name plates into cakes of transparent soap. A slit in one side of the soap cake is made with a sharp knife or a suitable slitting machine and the name plate is inserted into the slit.

Furthermore, it is possible to add to the still liquid soap small cuttings of very hard milled toilet soap, distributing them as fast as possible in the soap mass and pouring the soap into small-size water-cooled frames, where cooling proceeds rapidly. Thus, a kind of hard transparent figged soap may be obtained.

Perfumes used for transparent soaps may be the same as for common toilet but, as they are usually added at elevated temperatures they must be of the more alkali-resistant types.

Usually, 0.8–1.5% of the perfume composition is used. Some typical formulas are: (*a*) 75 oil of cloves, 75 oil of geranium (synthetic). (*b*) 150 oil of geranium, 20 oil of cloves, 75 oil of bergamot. (*c*) 125 oil of violet, 60 oil of geranium, 125 oil of bergamot. (*d*) 200 petit grain oil, 200 oil of geranium (synthetic), 100 oil of palmarosa, 100 gingergrass oil. (*e*) 40 oil of citronella, 40 benzyl acetate.

Colors for transparent soaps must be clearly soluble in water and resistant to alkali. To produce a certain fluorescence, 5–10 g. fluorescein may be used for 100 kg. soap.

The older concept of the *structure* of transparent soap was that common transparent soaps are quite isotropic and devoid of crystalline structure. They were considered essentially as undercooled amorphous soap gels.[49] I. Alexander found in the ultramiscroscope that slow cooling can produce large distinct crystals in a clear matrix. The soap thereupon becomes opaque, due to irregular scattering by the large randomly arranged crystals and clefts between them.

More recent investigations by Tyutyunnikov, Pleshkova, and Chernichkina[50] confirmed, in principle, the findings of Richardson. The Russian investigators used a polarizing microscope and found that the glassy condition of a transparent soap may represent a metastable system in which crystalliza-

[48] A. N. Ghose, *Soap, Perfumery and Cosmetics, 11,* 236 (1938).

[49] W. D. Richardson, *J. Am. Chem. Soc., 30,* 414 (1908). K. Mac Lennan, *J. Soc. Chem. Ind.* (Trans.), *40,* 27 (1921).

[50] B. Tyutyunnikov, Z. Pleshkova, and A. S. Chernichkina, *Seifensieder-Ztg., 68,* 193–194, 205–206, 215–216, 227–228, 237 (1941).

tion is inhibited by undercooling. McBain and Ross[51] investigated the problem again by submitting two samples of Pears soap to x-ray investigation. The first was a sample made in England twenty years ago and the second was one of recent manufacture, purchased in the United States. The two looked very similar in spite of the great difference in age. Both the old and the new bars of Pears soap gave an x-ray pattern that immediately proved that they were definitely crystalline; they were not even merely liquid-crystalline as far as the main material was concerned. By analyzing the x-ray diagram, McBain and Ross came to the following conclusion: The difference between ordinary opaque or semi-opaque soap and transparent soap consists essentially in the very much finer size of the crystalline particles of the latter. The bar is transparent because the extremely small crystalline particles are too small to provide optical discontinuities when compared with the wavelength of ordinary light. A transparent soap, such as Pears soap, is shown to consist of a mass of fine ultramicroscopic crystallites, scattering light and arranged completely at random. Storage for twenty years at room temperature does not appreciably affect this structure.

(3) Shaving Soaps

The following types of shaving soap preparations are on the market: (1) *Shaving bars* to be used with the old fashioned shaving cups, or sold in wooden mugs. Produced on similar lines are the less important *shaving powder* and the more modern *shaving stick*. (2) *Shaving cream*, produced along similar lines, and the less important *liquid shaving soap*. (3) *Brushless shaving cream.*

(A) Shaving Bars and Sticks

In principle, these soaps are produced from high-grade raw materials so that a boiling on niger becomes unnecessary and the ready saponified soap is simply "run." The method of manufacture is usually by the semiboiled process or by the cold process, the latter being less suitable.

The requirements of a good shaving soap are quick and copious lathering, softening effect on the hair, and no detrimental effect on the skin such as "biting" during application, during the actual shaving, or after the shave. Besides, the soap should not have a corrosive effect on the blade.

To meet these requirements, shaving soaps must be prepared from a properly balanced fat charge, properly saponified (no free alkali!), and they are usually superfatted with a certain amount of free stearic acid which is left unsaponified. For *solid* shaving soap, 2–3% free stearic acid is recommended. The saponification lye is a mixture of caustic potash and soda.

[51] J. W. McBain and S. Ross, *Oil & Soap*, 21, 97–98 (1944).

The proportion of NaOH : KOH is usually about 1 : 1 up to 1 : 2. The amount of coconut oil used should usually not be less than 20% of the fat charge. An addition of 3–8% glycerine is advantageous.

The following formulas are examples of shaving soap in *bar* form which may be run into forms, or the frames may be cut later on, or it may be pressed into wooden mugs or cups.

Ingredient	a	b
White tallow	600 parts	650 parts
White lard	200	—
Olive oil	—	100
Coconut oil	200	250
Caustic soda (38° Bé)	240	240
Caustic potash (50° Bé)	225	220
Glycerine	50	80

The melted fat charge is run into the crutcher, glycerine is added, and the lye mixture is run into the fat charge at about 70–80°C. Either the fat charge is saponified under constant but slow stirring in the crutcher or it may be saponified at boiling temperature with open steam. In this case, the lye mixture must be added in portions as described in the chapter on soap boiling (Chapter XVII). Usually, the semiboiled process is preferred. Should the mass in the crutcher become too thick, a small amount of potassium chloride solution (20° Bé) may be added.

Usually, the soap in the crutcher is adjusted so that the fat charge is completely saponified (a small sample withdrawn is clearly soluble in boiling distilled water) and a certain amount of free alkali remains. The free alkali is then neutralized with molten stearic acid, so that a surplus of 2–3% free stearic acid remains (see Chapter XXXIX, 5).

The above two formulas give soaps of the more old fashioned type. Especially when a high percentage of tallow and/or lard is used, the soap may tend to have a specific "soapy" odor. Under all circumstances only high grade white odorless tallow or lard should be used. To prevent this odor, high percentages of perfume have to be used. However, if a certain amount of sodium thiosulfate is added after saponification is complete, this odor does not arise. 0.5–0.75 sodium thiosulfate dissolved in equal parts of distilled water is added to the ready saponified soap before pouring into forms. The perfumes are also added at this time.

More modern types of shaving soaps are produced with fat charges containing high percentages of stearic acid. These soaps are usually white in appearance and are easy to produce by the semiboiled method, the most favored method for the production of shaving soaps:[52]

[52] E. G. Thomssen and C. R. Kemp, *Modern Soap Making*, MacNair-Dorland, New York, 1937, p. 202.

	A	B	C
Stearic acid	62 parts	400 parts	207 parts
White tallow	62	400	180
Coconut oil	132.5	900	108
Caustic potash (38° Bé)	—	90	108
(39° Bé)	88.5	—	—
Caustic soda (38° Bé)	—	175	—
(39° Bé)	85.0	—	—
(40° Bé)	—	—	132
Glycerine	20.0	50	—

The molten fat charge is run into the crutcher, glycerine is added, and the lye mixture is run into the fat charge with constant stirring at about 40–45°C. After the fat charge is completely saponified, the free alkali is neutralized with a surplus of stearic acid, and the ready soap is run into forms. A certain amount of 1% turkey red oil may be added to the adjusted soap before pouring.

Perfumes are added suitably, together with the turkey red oil in which the perfumes are soluble. To ensure complete homogeneity it may be advisable to pump the hot liquid soap from the bottom of the kettle and to reintroduce it at the top. In this case, care must be taken that the soap does not solidify in the pipes, or they become clogged and it is very difficult to free them again. The pipes should therefore be insulated and pumping should be carried out not below 80°C.

It is possible to produce shaving soaps in bar form by the cold process. However, this is not recommended, as it is impossible to adjust the free fatty acid content by addition of stearic acid. In order to produce a neutral superfatted shaving soap by the cold process it is only possible to calculate the saponification lye so that some unsaponified fat remains. However, this makes the soap much more liable to rancidity. Still, the method is often considered convenient. It is also possible to saponify the fat charge with the exactly calculated amount of caustic lye and to add 2–3% lanolin to the fat charge. In this case, the soap will be neutral and free lanolin or at least the unsaponified part of it, will remain as superfatting. The following are examples of cold-made shaving soaps to which lanolin is added as described:

	A	B	C	D
Coconut oil	11 parts	6 parts	9 parts	10 parts
White lard	—	3	3	—
White tallow	22	23	28	35
Castor oil	2	—	3	—
Olive oil	2	3	—	—
Caustic soda (38° Bé)	10	—	10	14
Caustic potash (38° Bé)	8	—	10	10
Sesame, peanut, or olive oils	—	—	—	5

The method of manufacture is as usual with cold-made soap (see Chap. XIX, 4). Usually the caustic soda is added first and then the caustic potash. The temperature of the fat charge is kept a few degrees higher than the melting point. After thickening, the mass is poured into frames, where the saponification process is completed. The perfume must be added to the fat charge. *No free alkali* should remain in the soap.

In certain cases, shaving bars may be made as follows. A soft potash soap is made by the semiboiled process and superfatted with stearic acid. This base is then added to a standard soda soap base of the proper fat mixture which has been dried and flaked to a moisture content of 12–14%. The ratio of soda soap base to potash base must be fairly high and may run 2 : 1. This mixture is amalgamated in the usual way, milled, and plodded. The plodded bars are then cut and pressed into the shaving mugs or cups, or into molds, and wrapped as refills for the mugs. The advantage of this process is that it gives a firm hard cake which lasts for a long time with very little shrinkage.

Some formulas for *shaving sticks* are as follows:

	A	B
Coconut oil	280 parts	25 parts
Stearic acid (triple pressed)	900	75
Glycerine	70	7
Caustic soda (35° Bé)	37	—
(38° Bé)	—	20
Caustic potash (50° Bé)	505	20

The molten fat charge is saponified with the lye mixture by the semiboiled method in the crutcher after the glycerine has been added. Complete saponification ensured, the eventual free alkali is neutralized with stearic acid so that 2–3% remains free. It is also possible to adjust the free stearic acid to 1% and to add 1–2% glyceryl monostearate. These soaps are usually pressed, milled, and plodded, as noted above, and the perfume is added during the milling process. About 0.2% titanium dioxide may be added to increase whiteness.

It is possible to produce *powdered shaving soap* from the dried flakes of such soaps. In this case the proportion of caustic potash and caustic soda may be changed, so that more caustic soda is used. However, formula *b* is well suited, as it stands for the production of powdered shaving soap. The flakes from this soap may be mixed with 25–35% of previously prepared dried tallow soap chips. 10% starch may be added as well. Powdered products have a large scale with commercial barber shops where their use is economical and sanitary. Certain types of electric lather dispensers operate entirely on powders.

(B) SHAVING CREAMS

More and more shaving soaps have been replaced by shaving creams. Convenience in use and quicker lathering properties, together with the pleasant appearance are the attributes of a properly prepared shaving cream. However, the production of a shaving cream is much more difficult than the production of a shaving bar or stick.

What are the qualities that are demanded nowadays in a good lathering shaving cream? First, the cream must quickly work up a thick, smooth lather. Second, it must not cause irritation of the skin at any time or leave the slightest unpleasant effect during and after the shave. Third, the cream should be of fine consistency and pleasing to the eye; one with a beautiful pearly luster is considered most desirable. To these qualities must be added that the cream must be practically unchanged in consistency at a temperature range of 15–38°C., the most difficult requirement to be fulfilled!

In order to produce a cream corresponding to all these requirements, two main points must be considered. First, the proportion of caustic soda to caustic potash—which ranges from 1 : 4 to 8 : 1. Second, the percentage of coconut oil in the fat charge—which ranges from 20% calculated on the fat charge as minimum up to 40% which we consider as maximum.

It is also recommended that neutral fat should be used, in small percentages only, with the exception of the coconut oil, which is generally employed as neutral fat. A certain amount of glycerine is recommended, 4–15%—calculated on the finished product.

Glycerine may be replaced by diethylene glycol monoethyl ether, which is claimed to have greater softening effect on the beard with less harsh effect on the skin, in addition to enhancing the shaving value of a ready lathering soap. Foam stability may be increased by adding 2–3% of sorbitol sirup after complete saponification of the fat charge.[53] The amount of free fatty acid—as stearic acid—should be adjusted between 4 and 6% (calculated on the finished product). The fat content should not be lower than 36% and not higher than 45%.

Some typical formulas for shaving creams are:[54]

I

30 parts coconut oil
73 parts stearic acid
48 parts caustic potash (37° Bé)
15 parts glycerine
9.5 parts caustic soda (38° Bé)
95 parts water

[53] M. J. de Navarre, *The Chemistry and Manufacture of Cosmetics*, Van Nostrand, New York, 1941, p. 428.

[54] J. Davidsohn and A. Davidsohn, *American Perfumer*, 38, 35 (1939). E. J. Better, *Deutsche Parf. Ztg.*, 18, 89 (1932).

II

130 parts stearic acid			135 stearic acid
35 parts coconut oil	} or {		35 coconut oil
14.5 parts white tallow			10 olive oil

56 parts glycerine
85.2 parts caustic potash (38° Bé)
15 parts caustic soda (38° Bé)
130 parts water
6 parts boric acid

We will discuss the second formula as an example. First, the coconut oil and the olive oil mixed with one third of the glycerine is saponified either separately by the cold method or in the crutcher by the semiboiled method with the whole amount of caustic soda and about 8.5 parts of caustic potash. After complete saponification (clear solubility in distilled water) the remainder of the glycerine, caustic potash, and 60 parts of water is added and the mixture is heated until a clear solution results. Then the molten stearic acid is run in and, during the process of adding the stearic acid, a previously prepared hot solution of boric acid in the remaining water is added. This keeps the mass in the kettle "open." During the whole process the agitator should work at about 10 r.p.m. to prevent aeration. After the whole process is finished, stirring is continued as long as possible and the soap is poured as a thick mass into large containers, usually of Monel or stainless steel. The cream is brought into cold storage or cellars where it is left for about a fortnight to "set-up" at a temperature of about 15°C. The cream is mixed every day or second day. During this storage process it changes consistency and becomes soft and creamy with a pearly luster. Perfume may be added at any time during this mixing process.

Such cream corresponds to all requirements of the Federal Specification for shaving creams, which is quoted in abridged form at the end of this section.

Addition of triethanolamine and turkey red oil is an asset as a regulator of consistency and because of the excellent properties these additions impart to the cream. They may be made part of the original formula. For example, in the formula above, 11 parts of stearic acid is saponified with 5.5 parts of triethanolamine in 11 parts of water at 80°C., stirred until a smooth transparent soap results, and added along with 1% turkey red oil (calculated on the cream) to the finished soap prior to the addition of the perfume.

Some difficulties arise when the free fatty acid content is adjusted with boric acid alone; this is due to the nature of boric acid itself. If 2% boric acid is added to a cream, fatty acid content as high as 5% may be found by titrating the free fatty acid directly on a sample of cream dissolved in neuralized alcohol, but only 2% free fatty acid is found if the unsaponified and unsaponifiable fatty matter previously extracted (according to standard

method) are titrated and redissolved after evaporating the petroleum ether in a neutral alcohol-ether (1 : 1) mixture. (Of course, the latter result is the correct one.) There seems to be an equilibrium between free boric acid and soap, and the splitting of soap by boric acid is not complete. Not all the boric acid reacts, but is later titrated as free fatty acid, which gives too high results.

It is very often of advantage to have in stock a shaving cream saponified *only* with caustic potash which may be added to a normal potash-soda cream in varying proportions during the perfuming process to regulate the consistency of the final cream. By adding this potash cream the proportion of K : Na may be adjusted somewhat, so that in case of difficulties of consistency it is not necessary to produce a new batch of shaving cream with altered K : Na proportion.

Another point is that, according to our experience, the total fatty acids separated from a good shaving cream usually show a neutralization value of about 210 and a titer about 48–49°C. According to Auch[55] titers of 50–52°C. were also found in popular shaving creams. Titers lower than 48°, however, will usually be found with shaving creams that may be quick lathering but do not show a thick creamy lather as in creams with high percentages of stearic acid.

Given below are some formulas of different authorities:

> 135 parts stearic acid
> 33 parts coconut oil
> 20 parts caustic soda, 36° Bé
> 84 parts caustic potash, 36° Bé
> 24 parts glycerine
> 165 parts distilled water
> 5 parts boric acid
> 14 parts triethanolamine
> 10 parts potash solution (18% K_2CO_3)
> 10 parts potash solution (40%)
> *500 parts total*

The cream is prepared as described below, starting with the lye mixture prepared as follows:

> 20 parts caustic soda, 36° Bé
> 84 parts caustic potash, 36° Bé
> 24 parts glycerine
> 14 parts triethanolamine
> 120 parts distilled water
> *258 parts total*

120 parts of this mixture is brought into the saponification vessel and heated to 80°C. In a separate vessel, 40 parts stearic acid and 33 parts coco-

[55] *Soap, 11,* 23 (March, 1935).

nut oil are melted and heated to 80°C. This fat mixture is run into the warm lye mixture with constant stirring and 10 parts of 18% potash solution is added. The temperature is kept at 90°C. Now 5 parts of boric acid dissolved in 45 parts of hot distilled water is added and, later, in 10 parts of 40% potash solution. The remaining warm lye at 80°C. and the remaining molten stearic acid are run into this thin liquid soap mass. The cream is adjusted with stearic acid to a free fatty acid content of 0.3–0.5%. After cooling to 30°C., a superfatting mixture composed of 4 parts lanolin, 5 parts glycerine, and 1 part lecithin is added to the cream and the perfume is added as well. The cream is stored for 2–3 weeks, being carefully mixed every 2 or 3 days.[56]

Another formula is given by Harry:[57]

Stearic acid	30.0%
Coconut oil	10.0%
Palm kernel oil	5.0%
Pure KOH	7.0%
Pure NaOH	1.5%
Glycerine	10.0%
Water	36.5%
Perfume	q.s.

The following two creams are built completely on fatty acids:[58]

(1)		(2)	
Coconut oil fatty acids	3.2	Myristic acid	10.5
Myristic acid	6.3	Palm oil fatty acids	7.0
Tallow fatty acids	9.5	Tallow fatty acids	7.0
Stearic acid	12.5	Stearic acid	7.0
Caustic potash (calc. as KOH 100%)	3.4	Caustic potash	2.8
Caustic soda (calc. as NaOH 100%)	1.0	Caustic soda	1.8
Triethanolamine	4.7	Triethanolamine	3.5
Glycerine	5.5	Glycerine	10.0
Water	53.9	Water	50.4

It is important that shaving soaps, especially shaving creams, are produced in corrosion-resistant kettles. Nickel or nickel-clad steel, stainless steel, or Monel are recommended as materials of construction.

Another important factor is that creams should be filled into tin tubes. During filling, no cream should come in contact with the outside of the tubes. The folds of the open end of the tube must be free from cream, otherwise corrosion at this end of the tube occurs. Closing of the fold, eventually with a

[56] Formula by K. Bergstein, *Ber. Schimmel & Co.*, Leipzig, 1938. The formula is very slightly modified by us to eliminate a typical German raw material which was present in the original formula in a percentage of 0.89%.

[57] R. G. Harry, *Modern Cosmetology*, 2nd ed., Leonard Hill, London, 1944, p. 218.

[58] J. Kalish, as quoted by K. A. Pelikan, *Soap, Perfumery and Cosmetics*, 11, 1019 (1938).

special clip or crimp is important as well. The closing cups must also fit tightly.

It is possible to produce a *liquid* or *semiliquid shaving* soap by diluting a shaving cream to a fatty acid content of 18–20% with distilled water plus 2–5% alcohol.

Shaving soaps and creams are perfumed according to the same principles as high grade toilet soaps. However, even greater care must be taken to avoid skin irritating ingredients. Special ingredients, such as menthol in summer or in hot climates, and camphor in winter or in cold climates, are quite useful as skin stimulants and skin soothing agents[58a] and are now well established additions to shaving creams.

(C) BRUSHLESS SHAVING CREAMS

Despite the fact that it is somewhat beyond the scope of this book to deal with brushless shaving creams, since they are soap products only in a limited sense, they are an important enough group to be included here.

In principle, a good brushless shaving cream is built up like a kind of vanishing cream: 18 parts stearic acid and 10 parts petrolatum are melted and added at 70°C. to a warm solution (60°C.) of 0.15 part (18%) ammonia in 72 parts water and 5–10 parts glycerine; the mixture is stirred until completely cold. The perfume is added to the finished product. The ammonia may be replaced either by 0.45 part caustic potash (pure KOH) or by 1.5 parts triethanolamine. Some of the petrolatum may be replaced by lanolin.

Stearic acid	50
Lanette wax	6
Paraffin (liquid)	12
p-Chloro-m-xylenol	2
Triethanolamine	6
Distilled (or deionized) water	140
Perfume	0.75
Menthol	0.2
Carbitol	6.0

The stearic acid and waxes are melted together and brought to 70–75°C.; p-chloro-m-xylenol, as a skin disinfectant, is added, and this mixture is stirred into the warm (70°C.) triethanolamine dissolved in water. Then the perfume plus menthol dissolved in Carbitol is added and the mass is stirred until completely cold.[59]

[58a] S. Alperin (A. Davidsohn), *American Perfumer, 50,* 167 (1947).
[59] *Chemist & Druggist, 126,* 702 (1937).

Desirable qualities in a brushless shave, according to Harry[60] are as follows: (1) should spread evenly, be smooth and free from lumps; (2) should possess a soothing, not an irritant action; (3) should show no separation of water; (4) should soften the beard; (5) should vanish ultimately, leaving the face with a soft feel. To these we would add that the cream must be easily removed from the razor and should not form clogging residues in the plumbing of the washroom.

(D) FEDERAL SPECIFICATIONS

Federal Specifications for shaving cream and soap (in an abridged form) (FFF-C641) are given in Table XXI-7.

TABLE XXI-7

DETAILED REQUIREMENTS FOR SHAVING SOAP

Type I	Classes A and B cake and stick		Class C powder	
	Min.	Max.	Min.	Max.
Matter volatile at 105°C., %	—	10	—	2
Matter insol. in hot 95% ethyl alcohol, %	—	0.8	—	0.8
Free alkali	—	None	—	None
Free fatty acids (calc. as stearic acid), %	—	1.0	—	1.0
Matter insol. in hot distilled water, %	—	0.4	—	0.4
Anhydrous soap (calc. as potash soap), %	87	—	96	—
Amount passing a No. 20 sieve, %	—	—	100	—

DETAILED REQUIREMENTS FOR SHAVING CREAM

Type II	Class A lather cream		Class B brushless cream	
	Min.	Max.	Min.	Max.
Moisture (toluene distillation method), %	—	50	—	70
Matter insol. in hot 95% ethyl alcohol, %	—	0.3	—	—
Free alkali	—	None	—	None
Free fatty acids (calc. as stearic acid), %	—	6.5	15	—
Matter insol. in hot distilled water, %	—	0.3	—	—
Anhydrous soap (calc. as potash soap), %	40	—	—	—

In addition to these detailed requirements the passage regarding consistency of shaving creams should be quoted, since this is one of the requirements most difficult to comply with:

A lather cream shall be a soft uniform cream or paste free from free alkali. It shall be of such consistency that it will not flow from the tube without pressure, not require undue pressure, to extrude it, and not lose its form when extruded from the tube. It

[60] R. G. Harry, *Modern Cosmetology*, 2nd ed., Leonard Hill, London, 1944, p. 219. See also A. Davidsohn, *Deutsche Parf. Ztg.*, *20*, 293 (1934).

shall distribute well into the bristles of the shaving brush and adhere to the face when applied thereto directly from the tube. It shall yield a copious lather that does not dry rapidly on the face and shall rinse readily from a razor blade. . . . When the packed tubes are kept at a temperature of 38°C. (100°F.) for 24 hours and then at a temperature of 15°C. (59°F.) for 24 hours, the material at the end of each 24-hour period shall be on the application of slight pressure extruded from the tube as a smooth mass without any change in consistency and without any hardening or separation of the ingredients.

According to these specifications, a *brushless cream* should be a soft uniform paste free from free alkali. It should remain soft in the tube, spread easily, lubricate the razor during the shaving process, soften the hair, and rinse readily from the razor blade.

(4) Shampoos

Washing the hair with a good soap shampoo is still considered the best prophylactic against diseases of hair and scalp. Of special importance is the removal of bacteria from the hair and scalp, and a good hair wash is the best way of achieving this end.

In spite of the modern soapless shampoos made with sulfonated fatty alcohols or other sulfonates, soap still retains an important place as a basis for a satisfactory shampoo.

The requirements of a good soap shampoo are as follows. (*1*) The shampoos should easily give a copious and thick foam even with cold or lukewarm water. (*2*) The shampoo should not be irritating to the skin and should not render the hair brittle. (*3*) After washing, the hair should be soft and should show a certain luster. (*4*) Any insoluble calcium or magnesium soap formed should not remain attached to the hair.

These requirements are to be fulfilled if the proper conditions (*e.g.*, no excess of free alkali) and the proper soap base are selected.

Soap shampoos are on the market in cake, powder, paste or cream, and liquid form.

(A) Shampoos in Cake Form

These are either cold-made soap tablets with a high percentage of coconut or palm kernel oil (see Chapter XIX on cold-made soap), or they are grained and milled toilet soap with at least 40% coconut or palm kernel oil within the fat charge. It is possible to incorporate a cold-made soap from coconut oil alone into a common toilet soap during the milling process, whereby a soap mixture is obtained which is easily worked during the whole milling and plodding process. Special ingredients may be incorporated into this soap, *e.g.*, tar, sulfur, etc. (see Chapter XXII on medicated soaps).

According to Thomssen,[61] hair tint soaps are made by this method and a

[61] E. G. Thomssen, *Soap*, *32*, No. 4, 48 (1946).

rather high percentage of approved aniline dyes of suitable shades and mordants are incorporated. If pine tar or other medicament is to be incorporated as well, this can also be added to milled soaps. It is customary to add about 5% of soapmakers' grade of pine tar and to color the soap black or dark brown by the addition of the proper soap color like lampblack, burnt umber, or a non-toxic black dyestuff.

(B) Shampoos in Powder Form

These are built on the basis of highly concentrated powdered soap which contains not less than 20% coconut or palm kernel oil in the fat charge. It is possible to blend a pure coconut oil soap with common toilet soap so as to give the soap powder with the required percentage of coconut oil. The soap base is usually mechanically mixed with the other ingredients, which may be alkaline salts with not too strong alkaline reactions, e.g., borax, sodium bicarbonate, sodium sesquicarbonate, complex sodium phosphates of low alkalinity such as sodium hexametaphosphate, sodium tetrapyrophosphate, or sodium tripolyphosphate (see Chapter IX on soap builders). Other ingredients for shampoo powders are color substances such as henna powder and aubepine powder. If a bleaching effect is desired, sodium perborate in percentages ranging from 5–50% may be incorporated into the powder mix.

Some formulas for shampoo powder follow:

> 70 parts powdered soap (with at least 20% coconut oil in the fat charge)
> 30 parts sodium bicarbonate and/or borax, sodium sesquicarbonate, etc.

The proportions of alkaline salts to powdered soap may range from 9 parts soap to 1 part alkaline salts, but should not be lower than 1 part soap to 4 parts of the other ingredients.

The following formulas, containing coloring ingredients, are taken from an article by Thomssen.[61] One formula gives a reddish cast to the hair, the other whitens it.

GOLDEN SHAMPOO

Toilet soap powder	25 lbs.
Borax	22 lbs.
Henna powdered	3 lbs.
Aubepine powder	1 oz.

SILVER SHAMPOO

Toilet soap powder	28 lbs.
Borax	22 lbs.
Aubepine powder	1 oz.

A shampoo powder with a strong bleaching effect is:

> 60 parts powdered soap (see above)
> 30 parts sodium perborate
> 10 parts borax

A basic formula for a shampoo containing extract of camomile is as follows:[62]

Borax	100 parts
Extract of camomile	25 parts

Mix, dry the mixture at a gentle heat and reduce to powder; then add:

Powdered soap	900 parts
Oil of camomile	0.3 part

It is also possible to incorporate oil of camomile into the powder mixture; 0.1–0.3% is usually enough.

It is unnecessary to give further formulas for shampoo powder. The principles of their composition and manufacture are simple and it is easy to modify the basic formulas to suit special requirement. Addition of 0.5–3% sodium phosphates of the polyphosphate type, tetrasodium pyrophosphate, helps to prevent lime soap sedimentation on the hair. In shampoos containing high percentages of water (liquid and paste shampoos) it is not advisable to add phosphates of the meta- or tetraphosphate type (Calgon or Quadrafos), since after long periods of storage they slowly revert to the common orthophosphates. Here, additions of tetrasodium pyrophosphates, or even better, potassium tetrapyrophosphate (0.5–2%) are more suitable.

(C) Shampoos in Paste or Cream Form

These are either opaque or transparent. The opaque types have very much in common in composition and method of manufacture with ordinary shaving cream and their manufacture is practically the same. Thus, we give only a representative formula and refer for the description of the manufacturing process to Section 3, B on shaving creams.

Olive (or peanut) oil	70 parts
Coconut oil	25 parts
Stearic acid	448 parts
Caustic soda, 38° Bé	27.5 parts
Caustic potash, 38° Bé	279 parts
Water	250 parts

After having saponified the fat stock completely and having adjusted the free alkali to near zero, 1.5% boric acid dissolved in some water is added to produce a certain amount of free fatty acids.

A transparent shampoo may be produced from a soft soap containing about 40% coconut oil. The fatty acid content of the finished soap should not be lower than 40%. Such soap may be produced by the usual method for making a soft soap (see Chap. XIX, 3) or by the cold or semiboiled process. In this case, even higher percentages of coconut oil are advisable.

[62] *Pharmaceutical Formulas,* Vol. II, 11th ed. *Chemist & Druggist,* London, 1944, p. 251.

Castor oil is another useful ingredient for producing a cold-made transparent paste shampoo. Castor oil is an excellent accelerator for the cold saponification process. A formula for a transparent paste shampoo with excellent properties produced by a modified cold saponification process is as follows: 50 parts coconut oil, 50 parts castor oil, 61 parts caustic potash (38° Bé). The shampoo is suitably prepared in a steam-jacketed kettle fitted with a stirrer. After thickening begins—usually very fast—steam is admitted to the jacket and 220 parts of warm water is slowly added—until a smooth homogeneous soap is formed. The alkalinity is adjusted to not more than 0.05% free KOH, suitably even less.

It is possible to produce transparent paste shampoos with a low *pH* with triethanolamine as well, using fatty acids in the fat charge:

> 60 parts stearic acid
> 40 parts coconut fatty acids
> 59 parts triethanolamine
> 41 parts water (distilled or deionized)

Dissolve the triethanolamine in water. Heat to 70°C. and let the melted fatty acid mixture heated to 70°C. run into the aqueous solution in an uninterrupted stream, with constant stirring. The result is a soft paste containing 50% fatty acids. Additions of 1–3% turkey red oil are advisable to every kind of shampoo paste, since it improves somewhat the resistance against lime soap formation.

(D) LIQUID SHAMPOOS

These are the most popular shampoos. The method of producing liquid shampoos is in principle the same as for the common liquid soaps and we refer to the corresponding section (Section 1). Some of the formulas for liquid soaps are suitable for liquid shampoos as well—especially the more concentrated types with a high percentage of coconut oil. Formulas for preparing ordinary liquid shampoos, and for some special liquid shampoos, are given below.

The following are used for the production of liquid shampoos of the common alkali-soap type.

I

Coconut oil	100 parts
Olive oil	60
Castor oil	30
Caustic potash lye (50° Bé)	85
Glycerine	100
Water (distilled or deionized)	525
Fatty acid content	*ca.* 20%

II

Coconut oil	100 parts
Peanut oil	15
Olive oil	10
Castor oil	10
Caustic potash lye (50° Bé)	60–62
Alcohol	50
Glycerine	50
Water	450
Borax	5
Fatty acid content	*ca.* 17%

It is possible to replace some of the glycerine or alcohol in the formula with propylene glycol and/or isopropyl alcohol. The above formulas may also be modified by adding less water to bring about a higher concentration.

A highly concentrated heavy shampoo is produced by the following formula:

Olive oil	80 parts
Coconut oil	30
Alcohol	40
Glycerine	18
Caustic potash lye (39° Bé)	67
Water	52

Another formula by Thomssen[61] is for an alcohol-free shampoo:

Coconut oil	181 parts
Caustic potash lye (28° Bé)	187.5
Sugar sirup (50 lbs. sugar to 50 lbs. water)	100
Borax	2.75
Perfume	3.5

Some practical suggestion and formulas for the production of liquid shampoos were given by Jannaway.[63] For the cosmetic chemist unskilled in soap-making, Jannaway recommends the use of ready-made coconut soft soap together with a little prepared olive oil soft soap. This gives an excellent shampoo when dissolved in water or a water–alcohol mixture. Other potential additives include small amounts of technical sodium hexametaphosphate* (for hard water areas), potassium carbonate, borax, glycerine, etc. A liquid shampoo of this type might be made along the lines of the following typical basic formula (all parts are by weight):

Coconut potash soap (shampoo grade)	35.0 parts
Olive oil soft soap	10.0
Glycerine	5.0
Alcohol	10.0
Perfume compound	0.2
Distilled water	40.0

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[63] S. P. Jannaway, *Perfumery & Essential Oil Record*, 36, 179 (1945).

* In aqueous solutions, hexametaphosphates slowly revert to orthophosphates.

The soap is dissolved in half the given quantity of hot water, the rest of the water being added cold. The glycerine and alcohol (incorporating the perfume) are then stirred in. The resultant liquid soap is stored for 2–3 weeks, then the clear liquid is drawn off from any sediment and filtered through diatomaceous earth.

When the base shampoo soap is to be prepared from fats and alkalis, a formula such as the following may be used:

Coconut oil	14.0 parts
Olive oil	3.0
Castor oil	3.0
Caustic potash (stick)	4.7
Glycerine	2.0
Industrial methylated spirit	4.0
Sodium hexametaphosphate, technical[a]	1.0
Perfume compound	0.4
Water, distilled or softened	68.0

[a] Better still, use 1% tetrasodium pyrophosphate or tetrapotassium pyrophosphate.

The potash is dissolved in 9 parts of the softened water and allowed to stand for a few hours. The clear lye is then run slowly into a steam-jacketed pan containing the previously melted oils. The lye must be added carefully, the rate of addition being controlled to prevent excessive effervescence. Control tests for in complete saponification or excess alkalinity should now be carried out and suitable adjustments made. After sampling and correction, the remaining portion of the charge is added, in similar fashion to the addition of lye, *i.e.*, slowly and gradually. If large quantities of water are added, lumps will form and float about in the thin soap solution. These lumps will disappear only after prolonged boiling and stirring. If possible, the speed of the stirring gear should be gradually reduced as the soap gets thinner, until at the finish the blades are revolving at about 20 r.p.m. The finished soap is allowed to cool in the pan, when it should be drawn off and stored in vats. Filtration *after* prolonged storage will give a clearer product still. When the soap is new, a creamy deposit always results which must be removed before bottling.

Using the procedure outlined above, another typical liquid shampoo may be made from:

Coconut oil	18.0
Castor oil	4.0
Caustic potash (calc. as 100%)	5.3
Borax	0.5
Glycerine	4.0
Perfume compound	0.3
Water, softened	68.0

The properties of liquid shampoos made solely from myristic acid and

caustic potash are described by Schaal[64] who points out that a liquid sham-poo containing 20% myristic acid as the only fat base has these require-ments: (a) to be absolutely neutral, or even to contain minute traces of free fatty acids; (b) to be superior foaming, also in hard water; (c) to have no disagreeable effect, such as itching of the skin or burning the hands of the hairdresser; (d) to have great economy in use, yet to cleanse perfectly the hair and scalp; (e) to leave the hair with a good, vital appearance; (f) to be produced at the lowest possible cost.

It is often desirable to improve the lime resistance of liquid shampoos by an addition of 2–5% turkey red oil or a suitable non-ionic detergent. In this case it is even possible to superfat the shampoo with an addition of 0.5–1% light-colored olein to make sure that no free alkali remains. In any case, filtration must be carried out with the necessary precaution in order to ensure complete clarity of the product before bottling. Here, the same principles should be adhered to as were described in the section on liquid soaps.

It is sometimes desirable to produce liquid shampoos with a low pH in order to avoid the effect of the free alkali or hydrolytically freed alkali on the scalp or hair. Very often the effect of alkalinity is greatly exaggerated, and we agree with Cornblatt[65] when he says:

> To be sure, good toilet soaps and shampoos contain a minimum or are merely free of (surplus) alkali. Nevertheless, in the use of soap with water there is hydrolysis and separation of the combination of fatty acids and alkali. So for all purposes the use of soap entails the exposure of the skin and hair to alkali. With good soaps, the amount of this alkali as measured by the pH of the solution is 8.5 to 10.5. This is not ex-cessive, except for a very few individuals or individuals with certain diseases of the skin. For normal skins, too much has been made of this alkali factor; it may be safely ignored if a good soap is used. With some diseases of the skin, the skin may be found to be sensitive to materials having an alkaline reaction: under these conditions the use of soap solution in any form is contraindicated. The normal pH of the skin is between 3 and 6, but after washing with soap the pH is 9 or even higher. Although the skin quickly re-turns to its normal pH it may be undesirable with certain diseases to alter the acid mantle of the skin.

Liquid shampoos can be produced with only slight alkalinity (pH 8.0–8.5) by using triethanolamine as the saponification agent for fatty acids. Some representative formulas follow for triethanolamine shampoos to which turkey red oil may be added.[66]

Coconut oil fatty acids	63 parts
Olein (red oil)	27
Triethanolamine	48
Water	60

[64] J. Schaal, *Seifensieder Ztg., 1936,* 695–696, quoted by K. A. Pelikan, *Soap, Per-fumery and Cosmetics, 11,* 1019 (1938).

[65] T. Cornblatt, "The Effect of Soap on the Hair," in *Medical Uses of Soaps,* M. Fishbein, ed., Lippincott, Philadelphia, 1945, p. 81.

[66] Anon., *Drug & Cosmetic Industry, 58,* 445 (1946).

The coconut oil fatty acids and olein are melted together and brought to a temperature of about 60°C. In another vessel the triethanolamine is gently heated with the water (60–70°C.) and then the fat mixture is added to it. After thorough mixing, the reaction takes place rapidly. When the reaction seems complete, 40 parts of water is added, the mixture is heated to about 90°C. again with thorough but slow mixing to avoid the formation of foam. The soap obtained should be completely clear, so that no filtration is necessary. If the soap is not clear, a little more triethanolamine may be added and mixed well. A part of the water can be replaced by alcohol. Perfume is stirred into the soap after cooling.

A second formula is as follows:

Olein, light colored and practically odorless	110 parts
Coconut oil fatty acids	80
Triethanolamine	100
Alcohol or half alcohol and half water	110

Some water may be replaced by glycerine and some alcohol may be replaced by isopropyl alcohol.

It must be mentioned that additions of previously prepared methylcellulose solutions in water (see Ch. XI, 2, B) are very effective thickening agents for liquid shampoos; 0.4–0.6% dry methylcellulose, calculated on the ready liquid shampoo gives a better "body" to the product. Even higher percentages of methylcellulose solutions may be added to paste or cream shampoos.

The same methods of clarification are used for liquid shampoos as for liquid soaps (see Section 1 of this chapter).

(E) SOME SPECIAL ADDITIVES. PERFUMING OF SHAMPOOS

Harris[67] enumerates the following "solubilizing and coupling agents" which may prove useful in preventing separation of the ingredients, *e.g.*, perfumes as the results of extremes of temperatures; they help to provide clarity of solution and help to bind perfumes and eventually used superfatting agents, etc.: ethyl alcohol, isopropyl alcohol, Carbitol (not over 5%), methyl Carbitol,* ethyl Carbitol, diethyl Carbitol,* Cellosolve,* diethyl Cellosolve,* butyl Carbitol,* butyl Cellosolve,* diethylene glycol* (and other polyglycols), diacetone, 2-methyl-2,4-pentanediol, *tert*-butyl alcohol, pine oil, terpineol, propylene glycol.

The same author gives a table of "conditioning agents." Since soaps, because of their alkalinity, sensitize the skin and scalp and make the skin dry, these conditioners are also mentioned in Chapter XXV, 1 (see also Section 1 of this chapter) dealing with superfatted and liquid soaps such as the following: Carbowax 1500 and its stearate, Carbowax 4000 and its stearate,

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[67] J. C. Harris, *Am. Perfumer*, 48, No. 11, 55 (1946).

* Many glycols and their ethers are considered unwise additions to cosmetics unless carefully tested for safety and nontoxicity.

diglycol laurate, diglycol oleate, diglycol stearate, ethyl stearate, octadecenol, glyceryl monostearate, glyceryl monoricinoleate, propylene glycol stearate, ethylene glycol monostearate, lanolin, lecithin.

The use of sequestering agents to improve clarity in liquid soaps is of even more importance in the manufacture of liquid shampoos and the section dealing with this material should be reviewed at this point.

In the case of powdered shampoos it is advisable to add the *perfume* composition to the powdered soap alone and then to add the other ingredients. In the case of cream or paste shampoos the perfume is added at a temperature not higher than 60°C. Perfume for liquid shampoos should be suitably dissolved in alcohol. If no alcohol is used as a main component, it is still advisable to dissolve the perfumes in a small amount of alcohol. Generally, for perfuming liquid shampoos, the same considerations are important as for common liquid soaps. But in the case of triethanolamine shampoos the precautions with regard to alkali resistance may be relaxed somewhat. The perfume composition usually varies between 0.2 and 0.5% (calculated on the final product).

MEDICATED SOAPS AND THE GERMICIDAL EFFECT OF SOAPS

(1) Introduction

Soaps found application in medicine and pharmacy very early in history, for it was soon recognized that they were not only detergents but also served as disinfectants and antiseptics. Here, we are speaking of soap *per se* as well as of its use as a carrier of special ingredients, for soap gained entry into the pharmacopoeias of various countries from both these standpoints.[68] Foremost among scientists responsible for the introduction of soap into medicine was Unna[68a] at the beginning of this century.

However, it is important to point out the relatively limited field of soap for medicinal use, because soap cannot act as a carrier for all medicaments, and it may possibly have a detrimental action in many skin diseases (see Chap. XXXII). By its nature, as a salt of a strong base and a weak acid, soap can be blended only with a limited range of medicaments and only the chemist can judge which will be tolerated by soap. In order to be of real value, the composition of a medicinal soap should satisfy both chemical and medicinal criteria. We plan first to consider medicinal soaps which do not contain special ingredients, the *sapones* of different composition, to be found in the pharmacopoeia of every country that has a pharmacopoeia of its own. Then we shall consider medicated soaps with special ingredients.

Before dealing with their composition, we should like to make some general observations on the advantages of soaps in pharmacy. These are chiefly: (*a*) The great cleanliness in use; after use, the last traces can easily be removed from the skin by washing with water. If water must not be used, soaps have naturally only limited value, but it is possible to rinse with alcohol. In contrast to the procedure with ointments, soaps are left to act upon the

[68] J. Davidsohn and A. Davidsohn, *Soap, Perfumery and Cosmetics*, 10, 400–404 (1937).

[68a] P. G. Unna, *Klin. Vorträge Nr.*, 252 (1885).

skin only for a short time. Plasters are preferred for permanent action.
(b) Economy in use; in comparison with ointments, soaps are used much
more sparingly. (c) Disinfectant action of soaps. (d) Stimulating action
of soaps upon the skin. By this is understood the stimulus to the physiologi-
cal functions of the skin.

Lesser[69] makes the following statement in regard to germicidal soaps.

> The principal use for a germicidal soap is in the preoperative scrub-up of the sur-
> geon and assisting personnel. The use of an effective soap of this kind for routine wash-
> ing by doctors, dentists, nurses, and others concerned with the care of the sick or in-
> jured should also provide an added means of preventing the spread of infection. In a
> broader aspect, there are those who feel that the use of a germicidal soap by food
> handlers, whether in food processing plants or public eating places, could help to lower
> the incidence of communicable diseases. Its use by those who perform personal services,
> such as that done by barbers and beauticians could serve a similar function with respect
> to prevention of infection.

Medicinal soaps must naturally be of high quality, that is to say, the oils
and fats used in their production must be exceptionally pure and fresh and on
no account rancid. As mentioned below, pure tallow and lard are preferred
among animal fats, and olive oil among vegetable oils, while linseed oil is fre-
quently used for soft soaps. The use of coconut oil is usually avoided be-
cause of the irritating action on sensitive skin (see Chapter XXXII). Coco-
nut oil is employed, however, in combination with other fats and oils—as it
is used for toilet soaps—for the manufacture of soaps that contain special
ingredients.

(2) The Germicidal Effect of Soaps

Before describing the manufacture and composition of different medicated
soaps it is important to review the *germicidal effect* of soaps. Bacteriologists
seem to agree that the main use of soap as a disinfectant is to *remove* the
germs by its effect as a detergent. McCulloch[70] in his text on disinfection
and sterilization, points out:

> The common procedure of washing the hands in soap and water is of the greatest
> sanitary significance. A mere estimation of the ability of soap solutions to kill bacteria
> does not evaluate the hygienic benefits derived from washing the body in soap and water.
> Bacteria are enmeshed in the soap lather and removed from the skin with the rinse
> water and, since they can no longer be a source of danger, it makes little difference
> whether they are dead or alive. A clean skin is able to free itself of many pathogens;
> a power not shared equally by a dirty skin.

[69] M. H. Lesser, *Modern Chemical Specialties*, MacNair-Dorland, New York, 1950,
p. 69.

[70] E. C. McCulloch, *Disinfection and Sterilization*, 2nd ed., Lea & Febiger, Phila-
delphia, 1935, p. 354.

Soap acts as a germicide as well, but the nature of this germicidal action is not yet quite understood. McCulloch[70] enumerates the following factors which influence the germicidal activity of soaps: (*1*) the fatty acid radicals present in the soap; (*2*) the state of saturation of the fatty acid constituents; (*3*) the temperature and the concentration of the soap solutions when applied to the bacterial cells; (*4*) the amount of foreign matter present.

Microorganisms vary considerably in their resistance to the attack of soap, possibly because the cell membranes vary in preventing the entrance of the soap solution into the inner cell. Some observers have pointed out that the action of soap is mainly effective on the fatty substances in the capsule of certain microorganisms. Research was carried out very early to establish the kind of soaps that are effective as germicides and against what microorganisms, but as it is impossible to quote from all these experimental papers we will confine ourselves to citing results from later publications. Bayliss[71] came to the following conclusions:

Pneumococci are especially susceptible to the action of certain unsaturated soaps, such as sodium oleate, linoleate, linolenate, clupanodonate. The other unsaturated soaps, as well as the hydroxylated and saturated soaps, are less effective in killing this organism. The bile salts and sodium salicylate (taken for comparison) require high concentrations to kill pneumococci. The sulfate ester salts are pneumococcicidal in concentrations of 0.01%.

Streptococcus lactis is more resistant to the action of soaps than the pneumococci. The effectiveness of soaps in killing the latter microorganism does not parallel exactly its effectiveness against the former. The two saturated soaps, sodium myristate and laurate, the unsaturated soaps, sodium oleate, linoleate, linolenate, clupanodonate, ricinolate, abietate, as well as two sulfate esters, sodium lauryl sulfate and oleyl sulfate, are very effective in killing this streptococcus.

Of a series of other compounds taken for comparison, only sodium diiodosalicylate and undecylenate are effective germicides in a concentration of 1% at *p*H of 8.0 using *Escherichia coli* as the test organism.

Sodium diiodosalicylate and sodium undecylenate are also effective against *Staphylococcus aureus* at a *p*H of 8.0. Sodium abietate is effective above a *p*H of 8.0.

The effect of soaps was tested against different microorganisms by Klarmann and Shternov[72] according to the U. S. Food and Drug Administration method, which is an *end method*. In other words, a bactericidal effect is shown when the last viable microbe of a suspension of microbes has been killed, thus eliminating the possibility of multiplication and restoration of a potential risk. This is in contrast to a *counting method* which enables the observer to follow the gradual decrease in the number of viable microbes over a period of time, *e.g.*, as a result of exposure to the action of an antibacterial agent. Klarmann and Shternov point out that this method repre-

71 M. Bayliss, *J. Bact.*, *31*, 489 (1936) (referred to by McCulloch, *loc. cit.*, p. 360).
72 E. Klarmann and V. A. Shternov, *Soap*, *17*, No. 1, 23–26, 70 (1941).

sents the more appropriate one and come to the following negative conclusions:

The F.D.A. technic employing besides *Eberthella typhosa* and *Staphylococcus aureus* three other test organisms, *viz.*, *Shigella paradysenteriae*, *Streptococcus* and *Trichophyton rosaceum*, has been applied to a study of (*a*) the series of potassium soaps of holomogous fatty acids, (*b*) a group of commercially available washing and toilet soaps, and (*c*) a number of "technical" soaps obtained by the saponification of fatty vegetable oils. For practical reasons, all tests were carried out at 37°C. Of the homologous series, only salts of fatty acids with eight to ten carbon atoms evidenced a germicidal efficacy of some note. Fatty acids of this description do not occur in fats and oils used in soapmaking. As expected, therefore, the antibacterial properties displayed by the commercial soap products tested, were not such as to entitle this kind of soap to any one of the following designations: "disinfectant," "antiseptic," or "germicidal." Thus the question posed: "are soaps germicidal?" must be answered in the negative.

However, attention was called to the comparatively unusual efficacy of resin soap with respect to staphylococci and hemolytic streptococci, and to the possibility of formulation, with the aid of rosin, soaps with enhanced antibacterial properties; but this is subject to further study. On the other hand, experiments by others, *e.g.*, McCulloch and Fuller[73] found soap to exert germicidal action against the swine erysipelas organism, killing in dilutions of from 1 : 100 to 1 : 110 in the presence of 5% pig manure. The prophylactic value of thoroughly washing the hands with soap and warm water after having been in contact with this organism should be emphasized. The soap used in these tests was Ivory soap in bars, but additional experiments indicate that other brands of household soaps possess approximately the same germicidal efficiency. This is especially important for veterinary practice.

In very extensive research, Stuart and Pohle[74] tested the germicidal effect of chemically pure soaps of different individual fatty acids and from different oils and fats as well as rosin. Also, alkaline soap builders were tested at different *p*H values and temperatures. Rosin soap showed germicidal activity; and the order of increasing germicidal activity of rosin acid soaps was as follows: dehydroabietic, abietic, dihydroabietic, tetrahydroabietic. There seemed to be a direct correlation between the amount of hydrogen in the rosin acid molecule and germicidal activity for the organisms tested. It is beyond the scope of this book to reproduce the numerous interesting tables that show the effect of soap against different microorganisms. Tables XXII-1 and 2 are representative illustrations for the experimental method used by Stuart and Pohle in their extremely interesting publication. The following conclusions were drawn from the results of this study against *Staphylococcus aureus*, *Escherichia coli*, and *Eberthella typhosa*:

[73] E. C. McCulloch and S. A. Fuller, *Am. J. Vet. Res.*, *2*, 77 (1941).

[74] L. S. Stuart and W. D. Pohle, *Soap*, *17*, No. 2, 34–37, 73–74; No. 3, 34–37, 73–74 (1941).

Rosin soap solutions were more active as germicides than equivalent concentrations of fatty acid soap solutions.

Mixtures of rosin soaps and fatty acid soaps were germicidally more active than the corresponding fatty acid soaps.

Soaps made from rosins produced from longleaf pine gum and slash pine gum, respectively, had equivalent germicidal activity.

Oxidation of the unstable rosin acids reduced the germicidal activity of the resulting rosin soap.

Soaps made from pyroabietic acid were more active as germicides than soaps made from gum rosins.

The sodium soaps of tetrahydro-, dihydro-, and freshly prepared abietic acids were more active as germicides than soaps made from gum rosins.

TABLE XXII-1

Germicidal Activity at 30°C. of Rosin and Fatty Acid Soap Solutions at pH 10.2 against *Escherichia coli* and *Eberthella typhosa*[74]

Soap solution, made from	Concentration of solution, %	Plate count					
		E. coli, exposure time, min.			*E. typhosa*, exposure time, min.		
		2	5	10	2	5	10
Slash pine rosin	2	0	0	0	0	0	0
Coconut oil	2	0	0	0	0	0	0
Slash rosin	1	5	2	0	2	0	0
Coconut oil	1	5	0	0	3	2	0
Oleic acid	1	576	192	6	52	54	23
Pyroabietic acid	1	0	0	0	0	0	0
Palm oil	1	2240	2240	2240	888	472	388
NaCl[a]	0.85	2432	2112	2112	2560	2560	2560
Phenol[b]	1	0	0	0	0	0	0
Phenol[b]	0.5	2112	896	96	1680	384	320

[a] Physiological saline, pH 7.0.
[b] Phenol tested in water solution at pH 6.2. Standardized according to Ruehle and Brewer, U.S.D.A. Circular 198 (Dec., 1931).

Coconut oil soap was germicidally more active against *Escherichia coli* and *Eberthella typhosa* than other soaps made from natural fats and oils. Against these two test organisms coconut oil soap had an activity equivalent to that of a normal gum rosin soap. Rosin soap was much more active germicidally than coconut oil soap when *Staphylococcus aureus* was used as the test organism.

Soaps made from lauric or myristic acids, the two principal constituents of coconut oil, were more active against *Escherichia coli* and *Eberthella typhosa* than coconut oil soap.

Increasing the pH of both rosin soap solutions and fatty acid soap solutions above that normal to the household and toilet soaps increased the germicidal activity of these solutions.

Solutions of alkalies and alkaline salts in concentrations that have a pH of 10 and 11 had only slight germicidal activity. Sodium hydroxide solutions did not become markedly germicidally active until the pH of the solutions exceeded 11 or the temperature was raised above 40°C.

TABLE XXII-2

GERMICIDAL ACTIVITY AT 30°C. OF FATTY ACID AND FATTY ACID–ROSIN SOAP SOLUTIONS
AT pH 10.2 AGAINST *Staphylococcus aureus*[74]

Soap solution, made from	Ratio of components by weight	Plate count[a]														
		1.0% soln.					0.5% soln.					0.25% soln.				
		Exposure time, min.					Exposure time, min.					Exposure time, min.				
		1	2	5	10	20	1	2	5	10	20	1	2	5	10	20
Slash pine rosin[b]	—	1	0	0	0	0	5	0	0	0	0	238	118	51	32	15
Coconut oil acids	—	23	8	8	6	2	104	76	39	23	10	248	116	88	57	12
Palm oil acids	—	2416	312	288	252	252	1152	1152	704	640	512	1408	1408	1152	768	704
Palm oil acids, coconut oil acids	—	576	320	111	97	36	640	256	127	124	54	704	502	438	134	56
Palm oil acids, slash pine rosin	3 : 1	176	9	6	1	1	704	92	48	42	——	320	244	132	96	26
Coconut oil acids, slash pine rosin	3 : 1	20	15	0	0	0	11	3	3	0	0	——	92	20	20	10
Palm oil acids, coconut oil acids, slash pine rosin	2 : 1 : 1	47	24	12	11	7	52	48	23	12	13	211	136	110	66	24

[a] Control plate count 3 to 4 thousand.
[b] Slash pine rosins used in all combinations.

The germicidal activity of all soap solutions increased as the temperature was raised from 25 to 45°C.

A solution of 0.5% rosin soap at pH 10.2 completely killed *Staphylococcus aureus* in 5 minutes at 30°C. Complete killing of *Escherichia coli* was accomplished in 2 minutes at 30°C. with a 2% solution of either rosin soap or coconut oil soap at pH 10.2.

Regardless of the germicidal effects noted with varying rosin and fatty acid soaps, the fact remains that soap's principal role is that of removing germs and other organisms from the skin and in this it is admirably suited. By no stretch of the imagination can soap itself be considered in the category of a bactericide, disinfectant, or antiseptic.

(3) *Sapo Medicatus* of the Pharmacopeia

The U.S.P. XIII prescribes under *Sapo Durus* (Hard Soap) a soda soap which is described as follows:

Hard Soap occurs as a white or whitish solid, in the form of bars, hard, yet easily cut when fresh, or as a fine, white or yellowish white powder. It has a faint odor, free from rancidity.

Hard soap is slowly soluble in water and in alcohol; more readily, however, with the aid of heat.

An aqueous solution of Hard Soap is alkaline to indicators.

The characteristics of the separated combined fatty acids are:

Solidifying point (titer)	18–23
Acid value	185–205
Iodine value	83–92

Drying loss in weight does not exceed 36% for the evaporated soap or 10% for the powdered soap; alcohol-insoluble material not more than 1%; limits for alkali or free fatty acids and alkali carbonates are as follows:

Dissolve 2.5 g. of Hard Soap in 50 cc. of boiling neutralized alcohol, filter while hot, and wash the filter thoroughly with boiling neutralized alcohol: the filtrate requires for neutralization not more than 0.2 ml. of 0.1 N sulfuric acid or not more than 0.2 ml. of 0.1 N sodium hydroxide, using phenolphthalein T. S. as the indicator.

Wash the filtered residue obtained in the determination of alkali hydroxides or free fatty acids with 50 ml. of boiling distilled water, cool, and titrate the aqueous filtrate with 0.1 N sulfuric acid, using methyl orange T. S. as the indicator. Not more than 2 ml. of 0.1 N acid is required.

These limits correspond to either:

Free NaOH	0.032%
Acid value	0.45
	(equal to 0.225% free fatty acids)
Na₂CO₃	0.424%

These figures correspond to the followng prescription of the *British Pharmacopoeia*, 1948, for *Sapo Durus*, which is a hard soap made only from a suitable vegetable oil or oils, or from fatty acids derived therefrom. The

British Pharmacopoeia, 1932, permitted only olive oil as the fat basis. Specifications are:

Unsaponified fat	not more than 0.8%
Free alkali as NaOH	not more than 0.04%. For free acids not more than 0.2 ml. of $N/10$ NaOH is used up for 10 g. soap in 100 ml. of neutral alcohol
Loss on drying in tablet form at 110°C.	not less than 20% and not more than 30%
Loss on drying in powdered form at 110°C.	not more than 5%

Even if U.S.P. XIII does not prescribe olive oil as the sole base and leaves some room for combination of different fats and oils, the surest way to produce *Sapo Durus* U.S.P. is by saponifying in the usual manner olive oil alone and salting out with brine solution. It is interesting to note that the *British Pharmacopoeia*, 1948, contains a specification for a curd soap *Sapo animalis*. The soap is to be prepared from purified solid animal fat. The specification gives a titer of the combined fatty acids of not less than 42°C., which corresponds to tallow.

Sapo Mollis Medicinalis (Medicinal Soft Soap) is the only soap included in the latest edition of the U.S.P. XIV, and is described as follows:

Medicinal Soft Soap is a potassium soap made by the saponification of vegetable oils, excluding coconut oil and palm kernel oil, without the removal of glycerine. Soft Soap may be prepared extemporaneously in the following manner:

The vegetable oil	380 g.
Oleic acid	20 g.
Potassium hydroxide	91.7 g.
Glycerine	50 ml.
Distilled water, a sufficient quantity to make about	1000 g.

Mix the oil and oleic acid, and heat the mixture to about 80°C. Dissolve the potassium hydroxide in a mixture of the glycerine and 100 ml. of distilled water, and add the solution, while it is still hot, to the hot oil. Stir the mixture vigorously until an emulsion is formed, using mechanical stirring if desired, then heat the mixture on a hot plate, with constant vigorous stirring, until it becomes homogeneous and a small portion dissolves completely in hot water, producing a clear solution. Add sufficient hot distilled water to make the soap weigh 1000 g., and incorporate the water in the soap until it is uniformly distributed and the soap is of the same consistency throughout.

The vegetable oil to be used in the formula given above may be corn, cottonseed, linseed, olive, soybean, or similar oils which have a saponification value not greater than 205, and an iodine value not less than 80. Since glycerine is added only to accelerate the saponification, it may be omitted if desired.

The quantity of potassium hydroxide given in the formula is based on an alkalinity equivalent to 85% of KOH. If the potassium hydroxide is of any other strength, a proportionately larger or smaller quantity should be taken.

It is self-evident that this soap may be produced on a large scale as well.

The soap is described as a soft, unctuous, yellowish white to brownish or greenish yellow, transparent to translucent mass. It has a slight, characteristic odor, often suggesting the oil from which it was prepared, and an alkaline taste.

An aqueous solution of Medicinal Soft Soap (1 in 20) is alkaline to indicators. Water content determined with the distillation method shall not exceed 52% by weight of the soap. Alcohol-insoluble substances shall not exceed 3%; free KOH not more than 0.25%. Alkali carbonates contained in the alcohol-insoluble substances from 5 g. soap shall, after dissolving in distilled water, require not more than 0.5 ml. of 0.1 N sulfuric acid *per gram* of the original soap weight. Methyl orange is used as indicator.

The characteristics of the liberated fatty acids are as follows:

Acid value	not more than 205
Iodine value	not less than 85

The *Sapo Mollis* of the *B.P.*, 1948, is soap made from potassium hydroxide and a suitable vegetable oil or oils, or with fatty acids derived therefrom. It yields not less than 44% of fatty acids of olive oil.

Total fatty acids	not less than 44%
Free alkali	not exceeding 0.056% (KOH), or
Free fatty acids	same as permitted for *Sapo Durus* (see above)
Unsaponified fat	not exceeding 0.8%

The same condition applies to the fatty acids of Soft Soap as for Hard Soap.

The points to be complied with are clearly evident from this specification. The *B. P.* does not give any directions for preparation.

(4) MEDICATED SOAP WITH SPECIAL INGREDIENTS

Very often *carbolic acid* (phenol), C_6H_5OH, is added to soaps, but its effect in soap is diminished considerably, so that other disinfectants should be added which do not lose their efficiency when incorporated in the soap or when used in combination with soap in solution. The fact that carbolic acid loses its germicidal effect in soaps was established as early as 1928 by Hampil,[75] who found that the soap apparently interferes with the action of the disinfectant rather than enhances it, as occurs with the higher phenols when less than 1 part of soap is present for each part of phenol or cresol. She suggested four possible explanations: (1) that a new chemical compound, which is nongermicidal, may be formed; (2) that the soap may act as a protective colloid for the bacterial cells; (3) that the soap may remove the phenolic substance from the solution in a definite partition coefficient ratio; (4) that other physicochemical factors may be operative. From her work, Hampil concluded that the phenols are unsuitable for the production of germicidal soaps due to the marked inhibitory effect of sodium oleate, sodium myristate,

[75] B. Hampil, *J. Bact., 16,* 287 (1928).

potassium palmitate, and potassium stearate on the bactericidal properties of phenol, *m*-cresol, *sec*-butylphenol, *n*-butylresorcinol, and *n*-hexylresorcinol.

Even though this fact has been established, phenol is still used, *e.g.*, in *carbolic soaps*, without improving in any way the germicidal effect of the soaps. Instead of phenol, *cresol* should be used, despite the fact that it has a relatively low germicidal effect in soap; any method is more suitable than the one using carbolic acid.

Cresylic acid (cresol), $CH_3C_6H_4OH$ (technical cresol contains all three isomers of cresylic acid), may be incorporated in a percentage of about 5% during the milling process in practically any soap base. The soap containing cresylic acid is usually colored red. The effect of cresylic acid in solution is quite different where the proportion of cresylic acid to soap is more than 1 : 1. This is seen from the fact that cresol–soap solutions are an established disinfectant of proved value found in the pharmacopoeias of all countries.

Cresol forms the basis for *Liquor Cresolis Saponatus* of the U.S.P. XIII, which may be prepared as follows:

Cresol	500 ml.
The vegetable oil	350 ml.
Alcohol	55 ml.
Potassium hydroxide	72.6 g.
Distilled water, a sufficient quantity to make	1000 ml.

Mix the vegetable oil and the alcohol. Dissolve the potassium hydroxide in 100 ml. of distilled water and immediately add the hot solution to the oil while vigorously stirring the mixture with a mechanical stirrer. Continue the stirring until a small portion of the soap dissolves in hot distilled water to form a clear solution. Add the cresol to the soap, stir until a clear solution is obtained, and add sufficient distilled water to make the solution up to 1000 ml.

If desired, 58.08 g. of the potassium hydroxide may be replaced by 37.05 g. of sodium hydroxide. It is also permissible to omit the alcohol, in which case the oil should be warmed to 85°C. before the addition of the solution of the alkali, and the mixture heated, if necessary, to complete saponification.

The amounts of potassium hydroxide and sodium hydroxide cited were determined on the basis of the official minimum percentages of strength, 85 and 95%, respectively. If either or both the hydroxides used should have a different percentage strength, corresponding changes in the quantities should be made.

It may be mentioned that, in preparing the Liquor Cresolis Saponatus, it is advisable to dissolve 1% (calculated on the oil used) of cresol to the oil and to add concentrated KOH (*e.g.*, 38° Bé) to the oil in the cold. After stirring, the mixture starts to spin and turns into a homogeneous cream. Then warm in a water bath, wait till a sample becomes clear in distilled water, and proceed as already described. Cresol acts as saponification cata-

lyst (see Ch. II, 8). According to our experience, this method of preparation is very fast and simple.

As a matter of fact the product can be manufactured on a large scale as well. Cresol solutions with soap are often marketed under the name of *Lysol*. The germicidal value of Lysol also varies according to the particular soap used in its preparation. Soaps made from linseed oil or castor oil give the highest values, while those made with oleic acid give the lowest.[76] Other results were obtained by Tilley and Shaffer[77] using *E. typhosa* with the Rideal-Walker technique at 25°C. The highest phenol coefficient was obtained with coconut oil soaps, the lowest with linseed oil and soybean oil soaps. This contradiction may be explained by the fact either that different bacteria were used or that different conditions (temperature, etc.) cause much different results.

Additions of *chlorocresol*, $CH_3C_6H_3(Cl)OH$, to soap are also possible, *e.g.*, 1–2% to milled soap. The use of dichloro-meta-xylenol (D.C.M.X.) in soap in a percentage of 2.5% was recently recommended by G. Gemmell.[77a] The effect was comparable with that of hexachlorohene (see below).

A very important addition to medicated soap is *pine oil*. It is obtained by steam distillation of the oleo resin from *Pinus palustris* Miller and certain other species. The grades best suitable for medicated soaps of pine oil soap disinfectant are colorless or pale yellow with a turpentine-like odor (specific gravity at 20°C. about 0.9; boiling range 200–220°C.). Pine oil is soluble in the usual organic solvents. In solid medicated soaps it may be used in a percentage of about 5%. According to Pickett and Schantz[78] pine oils are composed of the following resin constituents:

α-Terpineol, 50–60%; other terpineols, 15–25%; borneol, 5–10%; fenchyl alcohol, 5–10%; esters, 5–10%; ketones and phenols, 1–2%.

As pine oil is a good solvent, it may be used for the manufacture of solvent soaps as well (see Chapter XX, 1).

Pine oils are also used as powerful and agreeable-smelling disinfectants. They replace cresol emulsions very often. Usually, pine oil emulsions—or *soluble pine oil* as these products are often called—are produced on a rosin soap basis. 60–70% pine oil, 10–20% rosin soap (calculated as anhydrous soap), and not more than 10% water are good and efficient disinfectants. The rosin is suitably dissolved in one-fourth of the pine oil used and added at about 70°C. to the warm lye. Then the remainder of the pine oil is added.

[76] Martindale, *The Extra Pharmacopoeia*, Vol. I, 22nd ed., Pharmaceutical Press, London, 1941, p. 466.

[77] F. W. Tilley and J. M. Shaffer, *J. Infect. Dis.*, *37*, 359 (1925).

[77a] G. Gemmell, *Mfg. Chemist*, *23*, 63 (1952).

[78] O. A. Pickett and J. M. Schantz, *Ind. Eng. Chem.*, *26*, 709 (1934).

Sometimes part of the rosin soap is replaced by highly sulfonated turkey red oil. Two formulas for soluble pine oil are:

70 parts pine oil	70 parts pine oil
17 parts rosin (light)	11.3 parts rosin
6.4 parts caustic soda solution, 38° Bé	4.35 parts caustic soda solution, 38° Bé
6.6 parts water	6 parts turkey red oil
	8.35 parts water

The turkey red oil is added after saponification of the rosin. Its addition has the advantage that the product is less sensitive to hard water. The phenol coefficient of pine oil is 1.5–4 when tested against *E. typhosa.*

A very strong disinfectant that may be added to soap is *ti-tree oil.* The oil distilled from the Australian ti-tree, *Melaleuca alternifolia,* contains about 50–60% of terpenes, including cineole (up to 8%) and terpineol, the primary source of the odor. It is antiseptic and has been advocated as a nonirritant germicide for general and surgical use. It has a Rideal-Walker coefficient of 10, but there are also less efficient brands on the market. Ti-tree oil was found to have the following constants:[79]

Specific gravity	0.8985–0.8961
Optical rotation	+6.8–+7.4
Refractive index	1.4782–1.4790
Ester No.	4–7
Ester No. after acetylation	80–84

The usual very high germicidal potency—coupled with a complete absence of toxicity and irritation—is one of the oil's most valuable and individual characteristics. Generally, 2–4% of ti-tree oil is added to the toilet soap. The high disinfectant value makes it a favorable addition to shampoos. 3–4% of ti-tree oil is sufficient for liquid, powdered, and paste shampoos. As a rule, ti-tree oil is added in the crutcher for hard soap, in the mixer for powdered soap, and simply added to the liquid for liquid soap. Occasionally, in the last case, the percentage of ti-tree oil must be lowered in order to assure the clarity of the liquid soap. A representative formula follows:[80]

Oleic acid	7 parts
Ti-tree oil	3
Coconut fatty acid	12
Triethanolamine	10
Glycerine	2
Water	66

The addition of *tar* to soaps, especially shampoos, is very popular. For therapeutic purposes the chief grades are coal tar and wood tar, the former

[79] K. N. Richardson, *Soap, Perfumery and Cosmetics,* March, 1937.
[80] R. E. Goldsborough, *Manufacturing Perfumer,* through *Drug and Cosmetic Ind.,* **44,** 359 (1939).

being obtained by the dry distillation of coal and the latter by the dry distillation of various woods. Owing to certain unpleasant qualities of tar (odor, color, skin irritation, etc.), efforts have been made from the earliest times to isolate its pure therapeutic constituents and thus to eliminate unpleasant secondary effects. Efforts made to obtain a fairly uniform product (an important point in the case of such a widely used medicament as tar, owing to the possibility of exact dosing) have had a successful formulation in the patented product *Anthrasol* (German Pat. 166,975). Although it has a powerful odor, the color is pale and it is therefore suitable for light-colored soaps. The product is obtained from coal tar by treatment with sulfuric acid and oxidation agents followed by distillation.

The tar or tar product may be worked into the finished soap in the crutcher. In the case of cold-process soaps, it is blended with the soap mass before pouring into molds. In the case of liquid soaps it is usually dissolved in the saponification lye together with glycerine and a little alcohol.

The following formulas for tar soaps are from *Pharmaceutical Formulas*:[81]

BIRCH TAR SOAP

Birch tar	100 g.
Water	50 g.
Lavender oil	5 g.
Coconut oil soap	900 g.

TAR SOAP

I

Wood tar	10 g.
Coconut oil soap	90 g.

II (Unna's formula)

Wood tar	5 g.
Superfatted soap base	95 g.

For making coal tar soap, the best base to employ is a good milled soap. Coal tar soaps have been replaced largely by the wood tar variety, *i.e.*, birch tar (5–10%), and juniper tar. Before crutching the tar into the soap, it is usually neutralized with alkali, while in order to maintain a standard of intensity and permanence of color a small amount of aniline black is generally incorporated. After crutching, the soap is framed, slabbed, and milled in the usual way. A milled tar soap can be made by mixing 40 lbs. of yellow soap stock with 5 lbs. of tar.

Pine Tar, U.S.P. XIII, is also suitable for the preparation of tar soaps.

[81] *Pharmaceutical Formulas*, Vol. II, 10th ed., Forrester, ed. *Chemist & Druggist*, London, 1934, pp. 564–565.

It is a product obtained by destructive distillation of wood of *Pinus palustris* Miller, or other species of pine. It is a blackish brown, viscous liquid heavier than water, and with an empyreumatic odor and sharp taste. It is slightly soluble in water, and soluble in alcohol, chloroform, ether, acetone, glacial acetic acid, fixed and volatile oils, and in solutions of caustic alkalies. The principal constituents are turpentine, resin, guaiacol, cresol, methylcresol, phenol, phlorol, toluene, xylene, and other hydrocarbons.

Juniper tar, U.S.P. XIII, is suitable for incorporation in soaps as well. It is a dark brown, more or less viscid liquid with a smoky odor, acrid, and having a slightly aromatic taste (specific gravity 0.950–1.055 at 25/25°; refractive index 20°, 1.510–1.530). Juniper Tar is very slightly soluble in water, soluble in three volumes of ether, chloroform, amyl alcohol, glacial acetic acid, and in oil turpentine; it is partly soluble in alcohol or petroleum benzene.

It may be suitable to use tar in combination with a solvent to produce a solvent-tar soap. If this soap is used on the skin or scalp it should be borne in mind that such soap will have a strong fat-removing effect, which is of advantage in cases of oily skin, but not dry skin. Only small amounts of solvent, *e.g.*, turpentine oil, pine oil or isopropyl alcohol, should be used, so that the tar does not penetrate too deeply into the skin. Tar-solvent soaps are again a field in which the dermatologist and soap chemist should cooperate.

Salicylic acid is not a powerful disinfectant but has other valuable qualities to recommend it for skin cosmetics (*e.g.*, prevention of perspiration). A point to remember when preparing salicylic acid soaps is that they keep only when in the anhydrous or nearly anhydrous form. Milled salicylic acid soaps are therefore to be especially recommended.

Curd soap	25 kg.
Lanolin	0.5 kg.
Salicylic acid	2 kg.

The salicylic acid, curd soap, and superfatting agent are mixed together and put through the rollers three or four times. *Salicylic soap pastes* are prepared by incorporating the acid with a water-containing potash soap with a high petroleum jelly content.

Borax soaps are easily prepared, especially in the solid form. The borax content usually ranges from 5 to 10%, based upon the curd soap, and the borax is added only after saponification is complete. Borax soaps are very effective as a soap for dogs; here the percentage may be much higher.

Camphor soaps are on the market only in the solid or paste form. They are notable for affording exceptional protection against frost. The usual content of camphor is 5%, but this can be reduced to about 1% in the case of camphor soaps intended mainly for cosmetic purposes.

Sulfur, a highly popular addition, is used in the form of sulfur flowers or colloidal sulfur. The sulfur flowers may be added either to the caustic lye used in making the soap or to the manufactured soap mass. Potassium sulfide is used to prepare colloidal sulfur; it is dissolved in the minimum quantity of hot water and added in a proportion not exceeding 30% to the hot soap mass. The application of polysulfides in the saponification lye is described by German Patent 424,489. The proportion of sulfur in ordinary sulfur soaps ranges from 3 to 10%. Sulfur soaps are frequently prepared in combination with beta-naphthol, tar, glycerine and camphor. Also, they are frequently superfatted. The action of sulfur is weakly reducing and antiparasitic; sulfur-containing soaps are especially indicated for skin diseases such as acne, seborrhea, etc. Although amorphous and even crystalline sulfur is used, colloidal sulfur is more effective. The following formulas for different sulfur soaps may serve as examples:[82]

SULFUR SOAP

I

Sulfur	5 parts
Coconut oil soap	35 parts

II (Unna's formula)

Precipitated sulfur	10 parts
Superfatted soap base	90 parts

CAMPHORATED SULFUR SOAP

Precipitated sulfur	10 parts
Powdered camphor	5 parts
Superfatted soap base	85 parts

SULFUR TAR SOAP

Unna's formula

Precipitated sulfur	5 parts
Wood tar	5 parts
Superfatted soap base	90 parts

An important addition to medicated soap is *ichthyol*, frequently used in combination with sulfur. Ichthyol[83] is a viscous, almost black substance with a disagreeable odor, consisting chiefly of the ammonium salts of the sulfonic acids of an oil prepared from a bituminous schist. It contains not less than

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[82] *Pharmaceutical Formulas*, Vol. I, 10th ed. *Chemist & Druggist*, London, 1929, p. 517.

[83] *Extra Pharmocopoeia*, Vol. I, l.c., 621.

10.5% of organically combined sulfur, and sulfur as sulfates is not more than one-fourth of the total sulfur. It contains not more than 50% of water. Ichthyol is soluble in water, partly soluble in 90% alcohol and in ether, and miscible with glycerine and fixed oils. The following formula is given for a milled ichthyol-sulfur soap:[84]

Soap chips	28 lbs.
Ichthyol	4.5 oz.
Petrolatum	2 oz.
Zinc oxide	2 oz.
Flowers of sulfur	2 oz.
Chlorophyll (oil-soluble)	1.5 oz.
Medicated perfume	4 oz.

Formaldehyde soaps are good disinfectants and consequently enjoy wide popularity in hospitals and as a means of disinfecting sickroom utensils. An oxidation product of methyl alcohol, formaldehyde is a colorless gas, intensely irritating to the eyes. It is soluble in water and is sold commercially as a 40% solution under the name of *formalin*. The pungent odor and caustic action of formaldehyde are considerably weakened by the soap substance. In percentages of 1–2% (as 40% formaldehyde solution) formalin added to milled soap imparts to such soap better germicidal properties. Often, polymerized formaldehyde (paraformaldehyde) is used in percentages up to 5% as addition to milled soap. But the best known formaldehyde soap preparation is *Lysoform*, which probably consists essentially of an aqueous solution of formaldehyde and potash soap. *Liquid* formaldehyde-soap preparations must be stored in well-closed bottles, because of the ready volatility of formaldehyde. A formaldehyde-soap solution completely identical with Lysoform is prepared, according to Schrauth,[85] as follows:

30 parts of coconut oil is saponified by vigorous mixture with a solution of 8 parts of pure caustic potash in 20 parts of water and about 10 parts of spirits until a uniform, pasty, transparent mass is formed. Enough 40% formaldehyde solution is stirred into the still-warm soap to bring up the weight to 100 parts. A complete solution is formed at once and left to settle for some time. The alcohol is necessary to produce a readily soluble soap, since the alcohol-free preparation turns cloudy with water. If much free alkali is present in the alcohol-free aqueous solution, it remains clear for some time, but later deposits a dark sediment.

Formaldehyde soaps in *paste* form are less commonly encountered in commerce.

A very important group of additions to medicated soaps are the *mercury compounds*. Soaps containing mercuric iodide are the most common form of mercury soaps and go back to an old English patent of Thompson (No. 9591 of 1886). Mercuric iodide is dissolved in a hot aqueous solution of potassium iodide to form K_2HgI_4 and the solution is incorporated into the previ-

[84] M. A. Lesser, "Medicated Soaps," *Soap*, 20, No. 10, 35 (1944).
[85] Schrauth, *Medicamentoese Seifen*, Springer, Berlin, 1914, p. 75.

ously prepared curd soap chips. Mercuric chloride, $HgCl_2$, is more difficult to incorporate, as this salt may form the mercury fatty acid salt in the soap, which then splits up into mercury and fatty acid, making the soap no longer effective. Better results are obtained in soap with mercury oxycyanide, $Hg(CN_2HgO)$. Mercury soap is especially popular as a disinfectant in gynecology. It is usually applied solid and only rarely in the liquid form. The results of experiments with mercuric compounds in combination with soap are reported in the McCulloch text.[86]

The rather unusual effect of soap on the germicidal action of mercury was discussed by Hamilton,[86a] who found that, when admixtures of soap and potassium mercuric iodide or the so-called *diiodide of mercury* were tested on *Eberthella typhosa*, the soap merely acted as a vehicle, but upon *Staphylococcus aureus* the soap increased the germicidal action of dilutions of the mercury approximately three times. Hampil[86b] reported that a certain strain of *Staphylococcus aureus* required a 1 : 1,000 potassium mercuric iodide solution to kill in five minutes, but when 1% sodium oleate was present the organism was killed with a 1 : 300,000 mercury solution. Somewhat similar results were obtained with commercial soaps.

A special mercury compound, *Afridol*, sodium hydroxymercuri-toluate, $HO \cdot Hg(CH_3) \cdot C_6H_3COONa$, containing 53.5% mercury was patented by I. G. Farbenindustrie (German Pats. 216,828 and 233,437) and is suitable for incorporation in soap in small percentages (*e.g.*, 0.1%).

The following list of some less important additions to milled soap are given:

Ingredient	Percentages commonly used
β-Naphthol	5
Tannic acid	7–10
Eucalyptus oil	3–4
Thymol	3
Carvacrol	3
Salol	2–3
Potassium iodide	5
Resorcinol	4–5
Menthol[a]	2–3

[a] In dentifrice soaps more menthol is generally used.

A new germicidal ingredient, developed by Givaudan-Delawanna, Inc.,[87]

[86] E. C. McCulloch, *Disinfection and Sterilization*, 2nd ed., Lea & Febiger, Philadelphia, 1935, pp. 267–268.

[86a] H. C. Hamilton, *J. Am. Pharm. Assoc.*, 9, 597 (1920).

[86b] B. Hampil, *Am. J. Hyg.*, 13, 623 (1931).

[87] W. Gump, *The Givaudan*, March and April, 1945. The patents relating to G-11 are U. S. Pat. 2,250,480 (W. S. Gump) and British Pat. 545,648 (E. C. Kunz and W. S. Gump). Also U. S. Pat. 2,535,077, Dec., 1950 (to Sindar Corp., an affiliate of Givaudan Delawana).

is marketed under the name of G-11, or hexachlorophene, and is prepared by condensation of two molecules of 2,4,5-trichlorophenol with one molecule of formaldehyde in the presence of concentrated sulfuric acid, as shown in the formula:
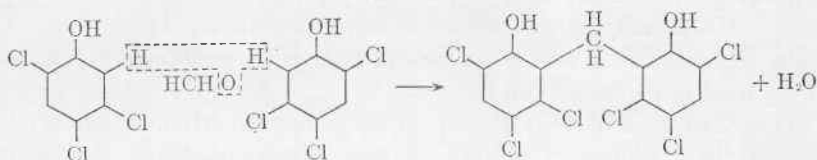
forming the compound bis-(2-hydroxy-3,5,6-trichlorophenyl)methane. G-11 is a white, crystalline substance, melting at 164–165°C. It is practically insoluble in water, but soluble in alcohol, acetone, and dilute alkalis. When tested in the form of its monosodium or potassium salt, this compound is strongly bacteriostatic and bactericidal against *Staphylococcus aureus* and other Gram-positive bacteria, but is of considerably lower activity against Gram-negative microorganisms such as *Eberthella typhosa* and *Escherichia coli*. Its phenol coefficient against *S. aureus* at 37°C., determined by the Food and Drug Administration method of Circular No. 198, is approximately 125. The substance is relatively nontoxic, with a minimum lethal dose for guinea pigs of about 300 mg. per kilogram body weight. Very extensive research shows that G-11 used in a percentage of 2% in milled soap has a strong germicidal effect. It is beyond the scope of this review to go into details of the tests employed to prove the efficiency of a 2% G-11 toilet soap, but the evidence brought forward by well-known bacteriologists[88] seems to justify the conclusion that the compound G-11 is a great step forward in the development of a germicidal toilet soap useful for the general public and for the medical profession as well. A retail product (Dial-Armour & Co., Chicago) containing the ingredient has met with outstanding success on the American market and it is being used in shaving creams. The Sindar Corp., an affiliate of Givaudan-Delawanna is licensing their U. S. Patent 2,535,077 to interested parties.

Very probably this is the most important germicidal additive available today for soap use. McCord[89] also includes mercuric iodide in this category.

With the advent of hexachlorophene interest in disinfectant soaps became much greater. It became more and more important to define the term "disinfectant soap." Pritchard[89a] proposes the following definition: "A soap is to be considered disinfectant if a 5% to 10% solution can be shown to kill

[88] E. F. Traub, C. A. Newhall, and J. R. Fuller, *Surg. Gyn. Obst., 79,* 205 (1944). H. J. Udinsky, *J. Med. Soc. New Jersey, 42,* No. 1, 15 (1945).

[89] C. P. McCord, *Ind. Med.,* 17, 421 (1948).

[89a] H. Pritchard, *Mfg. Chemist, 23,* 227 (1952).

mixed skin culture at 37°C. in the presence of organic matter." The same authority gives detailed methods for testing disinfectant soaps.

(5) Soap Liniments

Two official prescriptions for liniments built on the basis of soap are given. They are taken from *National Formulary VII* (1942).

COMPOUND LINIMENT OF SOFT SOAP

Soft soap	150 g.
Juniper tar	20 g.
Alcohol, a sufficient quantity to make	1000 ml.

Soften the soap by warming it in a dish on a water bath; remove it from the heat, mix it with 750 ml. of alcohol, and when it has dissolved add the juniper tar. Then filter the liquid, and wash the filter with sufficient alcohol to make the product up to 1000 ml. Mix well.

CAMPHORATED SOAP LINIMENT

Monohydrated sodium carbonate	10 g.
Stearic acid	50 g.
Camphor, in coarse powder	25 g.
Water	100 ml.
Oil of thyme	3 ml.
Oil of rosemary	6 ml.
Dilute solution of ammonia (10%)	50 ml.
Alcohol, a sufficient quantity to make	1000 ml.

Dissolve the monohydrated sodium carbonate in the water with the aid of heat, add 200 ml. of alcohol and the stearic acid, and heat the mixture until effervescence has ceased and solution results. Add the oils and camphor, dissolved in 500 ml. of alcohol, then the dilute solution of ammonia and sufficient alcohol to make the product measure 1000 ml. Mix well, and filter the liniment while warm. Pour the filtered liquid into dry, wide-mouthed bottles, stopper, and set aside to cool.
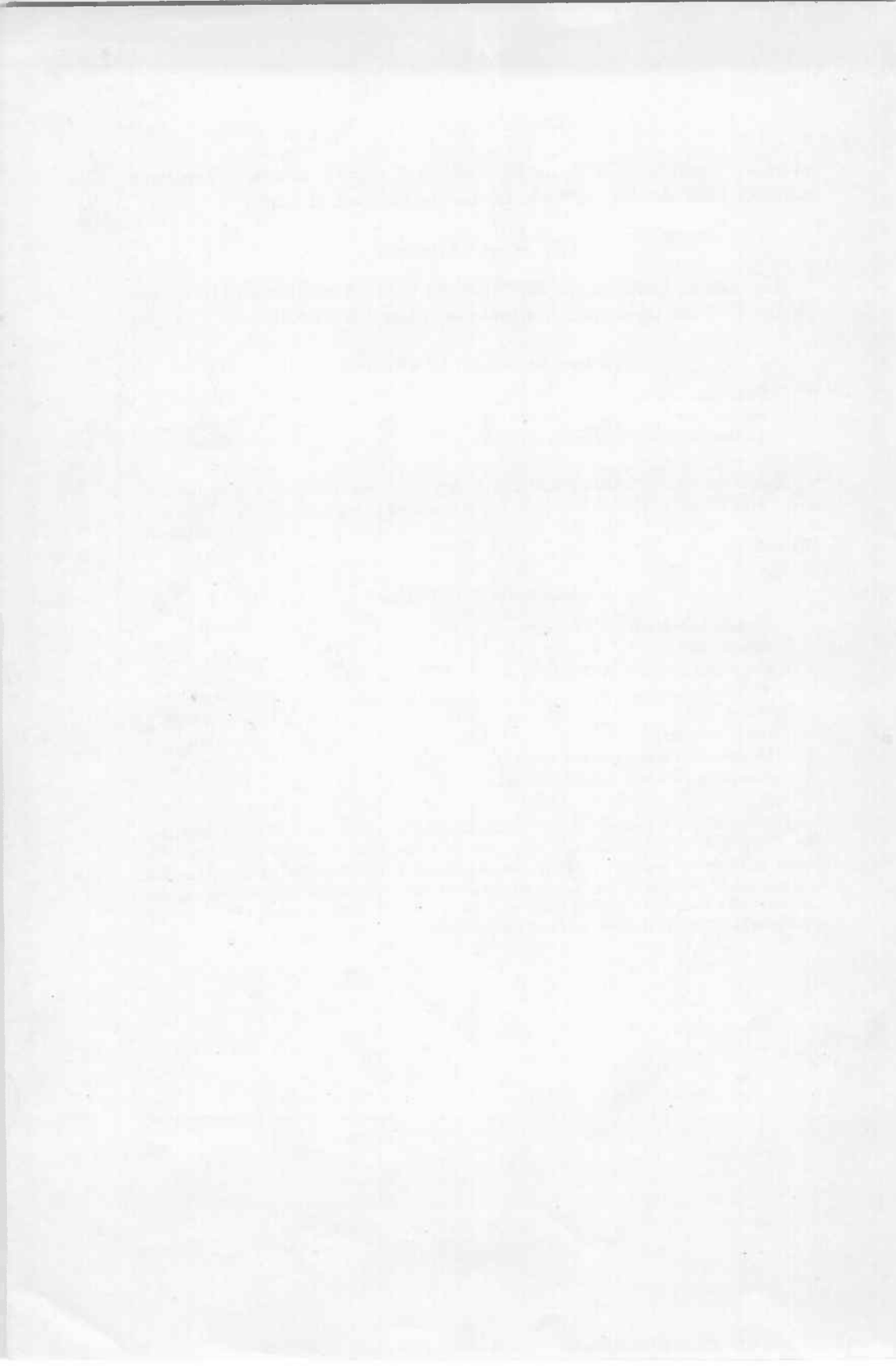
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